technical Report

Belvoir RD&E Center
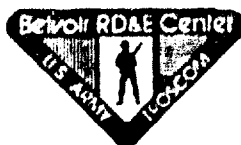
United States Army
Belvoir Research, Development & Engineering Center
Fort Belvoir, Virginia 22060-5606

Report 2478

The Prediction of Middle Distillate Fuel Properties Using Liquid Chromatography-Proton Nuclear Magnetic Resonance Spectroscopy Data

Authored By: **Dr. Madeline Swann**

Report Date: **June 1989**

Distribution unlimited; approved for public release.

REPORT DOCUMENTATION PAGE		Form Approved OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS None
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Distribution unlimited; approved for public release.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION Belvoir RD& E Center Fuels & Lubricants Division	6b. OFFICE SYMBOL (If applicable) STRBE-VF	7a. NAME OF MONITORING ORGANIZATION
6c. ADDRESS (City, State, and ZIP Code) Fort Belvoir, VA 22060-5606		7b. ADDRESS (City, State, and ZIP Code)
8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO. 627.33	PROJECT NO. AH20VM	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
The Prediction of Middle Distillate Fuel Properties Using Liquid Chromatography-Proton Nuclear Magnetic Resonance Spectroscopy Data (U)

12. PERSONAL AUTHOR(S)
Dr. Madeline Swann

13a. TYPE OF REPORT Final	13b. TIME COVERED FROM 1987 TO 1988	14. DATE OF REPORT (Year, Month, Day) June 1989	15. PAGE COUNT 60

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Middle distillate fuels, Liquid chromatography, Proton nuclear magnetic, ASTM test methods, resonance spectroscopy, Physical properties, chemical properties, Average molecular composition data

19. ABSTRCT (Continue on reverse if necessary and identify by block number)

The research was initiated to support the Army's capability to identify the components of fuels which contribute to low temperature performance of fuels. Once the research had begun, it was discovered that various physical properties of middle distillate fuels can be predicted. The LC-^{1}H NMR technique was developed to predict physical properties based on chemical structures present in the fuels. The prediction of properties is approached from a "group property" point of view. In the group property approach, the structure of the molecule is examined for structural features which dicate the physical properties of the compounds. In other words, the physical properties of a molecule or compound are determined by the number of types of chemical groups, i.e., methyl, methylene, methine, etc., present. These LC-^{1}H NMR predicted property measurements were compared to measurements obtained by the ASTM fuel tests. Most measurements were found to be within experimental error,

(Continued)

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT [x] UNCLASSIFIED/UNLIMITED [x] SAME AS REPORT [ ] DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Herbert K. Pollehn	22b. TELEPHONE (Include Area Code) 703-664-3576	22c. Office Symbol STRBE-VF

DD Form 1473, JUN 86   *Previous editions are obsolete.*   SECURITY CLASSIFICATION OF THIS PAGE

The research has demonstrated that the LC-^{1}H NMR approach for measuring various middle distillate fuel properties can be used as an alternative to the ASTM methods of fuel property measurement. It has been shown that it is possible to predict 17 physical properties with most of the predicted properties within the experimental error of the measurements obtained by the ASTM fuel tests. In addition, the LC-^{1}H NMR approach offers other advantages over the ASTM test methods. From this research, it can be seen that many physical properties can be determined in approximately 1 to 2 hours with approximately 3 to 5 milliliters of sample fuel. To determine the same properties by ASTM test methods, it would take approximately 50 hours and approximately 1 to 3 liters of fuel.

ii

TABLE OF CONTENTS

Page

TABLES

EXECUTIVE SUMMARY

The research was initiated to support the Army's capability to identify the components of fuels which contribute to low temperature performance of fuels. It has been observed in the field that the quality of fuels can have serious consequences on the Department of Defense (DOD) mission by degrading vehicles, equipment, and weapons components. It is mandatory that all factors influencing operability be understood because it is essential that DOD's mission not be unduly influenced by short-term fluctuations in petroleum supplies.

Although this research was initiated because of cold weather operability problems in vehicles and equipment, it was discovered that various physical properties of middle distillate fuels, including the cloud point, can be predicted. The liquid chromatography-proton nuclear magnetic resonance spectroscopy (LC-^{1}H NMR) technique developed can predict the following physical properties: cetane number (ASTM D613), cetane index (ASTM D976), density (ASTM D1298), specific gravity (ASTM D1298), pour point (ASTM D97), flash point (ASTM D93), viscosity (ASTM D445), filterability (ASTM D4539), heat of combustion (ASTM D240), cloud point (ASTM D2500), volume percent aromatics (ASTM D1319), residual carbon content (ASTM D524), and initial, 10%, 50%, 90%, and end boiling points (ASTM D86). It was also discovered that this technique provides chemical insight concerning the influence of chemical changes on the physical properties of the fuel. This led to expansion of the initial research goal. Therefore, the revised goal was to develop a simple analytical technique which can be used to rapidly predict various physical properties of fuels.

The LC-^{1}H NMR technique is now being developed to predict various physical properties of middle distillate fuels based on a single analytical technique. This methodology determines the average molecular composition data of the monocyclic and dicyclic aromatic, fluorene, and phenanthrene fractions. It also determines the fraction of total carbon for the alkane fraction. Finally, it determines, where applicable, the fraction of total carbon for the tricyclic or aromatic fraction. The on-line LC-^{1}H NMR data is also analyzed to give the following results: the molar quantities of each type of hydrogen and carbon present in the fuel samples, an average structure for each chemical class, and an average molecular structure for each class. Also, the ^{1}H and ^{13}C NMR analysis provides aromaticity data.

Once the LC-^{1}H NMR and ^{13}C NMR data is collected and analyzed, the process of predicting physical properties begins. This is the process of determining the relationship between chemical structures such as alkanes, monocyclic aromatics, dicyclic aromatics, etc., and physical properties such as cloud point, density, cetane number, etc. The prediction of properties is approached from a "group property" point of view. This group property approach of using chemical properties to calculate physical properties of classes of compounds has been utilized by chemists for several years. In the group property approach, the structure of the molecule is examined for structural

features which dictate the physical properties of the compounds. In other words, the physical properties of a molecule or compound are determined by the number of types of chemical groups present such as methyl, methylene, methine, etc.

The LC-^{1}H NMR approach was used in the chemical fingerprinting of middle fuel samples. A general predictive equation, based on the average molecular properties of each class of compounds present in the fuels, was developed. Using this equation, 17 physical properties of middle distillate fuels were predicted. These LC-^{1}H NMR predicted property measurements were compared to measurements obtained by the American Society for Testing and Materials (ASTM) fuel tests. Most measurements were found to be within experimental error.

The research has demonstrated that the LC-^{1}H NMR approach for measuring various middle distillate fuel properties be used as an alternative to the ASTM methods of fuel property measurement. It has been shown that it is possible to predict 17 physical properties with most of the predicted properties within the experimental error of the measurements obtained by the ASTM fuel tests. In addition, the LC-^{1}H NMR approach offers other advantages over the ASTM test methods. From this research, it can be seen that many physical properties can be determined in approximately 1 to 2 hours with approximately 3 to 5 milliliters of sample fuel. To determine the same properties by ASTM test methods, it would take approximately 50 hours and approximately 1 to 3 liters of fuel.

SECTION I. BACKGROUND

This research project was initiated because of cold weather operability problems in vehicles and equipment. When there are operability problems, the fuel is usually considered to be the source of these problems. Actually, low temperature operability of vehicles and equipment is a function of the following inter-related variables:

- Vehicle/equipment fuel system design
- Fuel composition
- Mode of operation
- Housekeeping or user/field practices

Cold weather inoperability occurs as a result of these variables individually and/or collectively not being adequately considered. When this research began, the major emphasis was on diesel fuel composition and its effects on low temperature operability of vehicles and equipment.

The manner in which diesel fuels are blended at the refineries from a diesel fuel pool and the sources of crude stocks will control their low temperature properties.[1] Fractions that contain normal and/or branched paraffinic hydrocarbons will have poorer low temperature properties because of the tendency for these waxy/paraffinic hydrocarbons to precipitate and become insoluable as the temperature is decreased. All diesel fuels contain normal paraffins with chain lengths varying from 10 to 25 carbon atoms (C_{10}–C_{25}). At low temperatures, some of the paraffins (C_{10} or higher) precipitate as wax crystals.

The wax content will vary due to refinery processes used by different refineries and the crude feedstocks. For example, Grade DF-2 diesel fuels usually contain 6 to 8 percent paraffin wax, depending on the refinery. Most refineries are not able to remove all of the normal paraffin hydrocarbons without greatly reducing product yields. Furthermore, removing too many paraffins will lower the cetane number of the resulting fuels, as well as affecting other properties such as gravity, viscosity, etc., which are essential for diesel engine performance.

Generally at or above 20°F, the wax will be in solution; however, at low temperatures, some of this wax will precipitate out since the solubility of the wax is a direct function of temperature. Therefore, the manner in which the diesel fuels are blended at the refineries will control their operability at low temperatures.

When wax crystals first begin to precipitate, they appear as a dispersed cloud, called the *cloud point*. It is at this point that fuel operability problems may first occur.[2] Therefore, the cloud point is the most important test property for defining low temperature operability of diesel fuels. It is when the ambient temperature approaches the cloud point of the fuel that the potential for vehicle/equipment inoperability will probably first occur.

Although these paraffin waxes can be troublesome, they also provide major benefits to the resultant fuel blend. They improve necessary ignition quality because the cetane numbers of the normal paraffins are high. (The cetane number affects the ability of the engine to start and the interval before it runs smoothly.) Their volumetric heat content is relatively high which also contributes to better fuel mileage and overall engine power.

Satisfactory low temperature operability of Army materiel is obviously a critical performance parameter. Fuels can contribute significantly to operational problems because the formation of wax crystals can lead to filter plugging, fuel line waxing, and/or nozzle fouling. This is significant in the area of operational readiness and combat effectiveness of military ground equipment. The past several years have generated numerous queries and requests from the field user for solutions to fuel waxing problems.

If the diesel fuel available causes low temperature operability problems, the vehicles and equipment can be winterized by changing the following:

- Equipment
- Equipment storage
- Operating conditions
- Fuel storage or
- Fuel itself.

The fuel can be winterized using procedures published in the US Army Belvoir RD&E Center Technical Report No. 2410 (AD-A144-710), *A Field Blending Guide for Improving the Low Temperature Properties of Ground Fuels* (June 1984). The fuel can be blended with low cloud point fuels and solvents—such as kerosene, JP-5, JP-8, Jet A, Jet A-1, High Flash Point Calibration Fluid, and Dry Cleaning Solvent, Type II—to effectively dilute the total wax content of the fuel to be used. The fuel should not be blended with MOGAS or JP-4 because of increased operating hazards associated with blending diesel fuel with gasoline and JP-4. These hazards include lowered flash point, increased probability that vapor space above the fuel will contain an explosive mixture, and increased evaporate emissions from the fuel tank, especially if recent engine operation has heated the fuel by recirculation. It is essential that blending be done before the onset of any anticipated low temperatures because complete mixing of the two fuels must occur in order to effectively lower the cloud point. Blending DF-2 with these fuels and solvents has eliminated low temperature operability problems in the past.

Another approach to solving the low temperature operability problems of diesel-powered vehicles and equipment is substituting JP-8 or JP-5 turbine fuel for DF-2 diesel fuel. In consonance with this substitution, DOD Directive Number 4140.43[3] was issued. This directive now states that combat and combat support vehicles and equipment shall be capable of achieving acceptable operational performance using either kerosene-type turbine fuels or distillate-type fuels and their commercial

2

equivalents. The conversion from DF-2 to JP-8 is currently taking place in Europe. This conversion is scheduled to be completed by FY91.

Although DF-2 can be winterized or JP-8 substituted, it is still essential to understand the wax crystal precipitation properties of diesel fuel at low temperatures. This is because during wartime, vehicles and equipment must be able to operate on commercially available and/or alternate fuels.

In an effort to develop a method to relate the cloud point of diesel fuels to the hydrocarbon species in the fuels, the continuous flow liquid chromatography (LC)-proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and static carbon (^{13}C) NMR methods of analysis were used to analyze diesel fuel samples. The first continuous flow LC-^{1}H NMR experiments were reported in 1979.[4] During the last 5 years, this technique has evolved into a new analytical tool for rapid structural elucidation of components present in complex mixtures. Demonstration of LC-^{1}H NMR as a quantitative analytical tool was first reported in 1982,[5] and a review of this technique was recently published.[6]

The initial LC-^{1}H NMR studies were hindered by signal-to-noise limitations of the electromagnetic-based NMR systems. However, the use of high field superconducting NMR magnets has alleviated the sensitivity problems. At the present time, continuous flow detection limits for a single compound in a complex mixture is 10 to 20µg for molecules of molecular weights of 100 to 300 daltons (200 MHz ^{1}H NMR). Also, these superconducting NMR systems have greatly increased the number of resolution elements in a given LC-^{1}H NMR spectral profile. This is not only due to increased chemical shift dispersion (for example, 100 MHz vs. 400 MHz -^{1}H NMR spectra), but also due to better main magnetic field (Bo) homogeneity of the superconducting magnet and technical improvements in flow cell design. Currently, continuous flow NMR linewidths of 0.5 to 1 Hz are easily achieved.[7]

During the development of the technique, a major problem envisioned for the LC-^{1}H NMR technique was the limited choices of chromatographically and/or NMR acceptable solvent systems which could be used without extensive background signals in the ^{1}H NMR spectra. This problem was solved by the use of the following:

● Deuterated, chlorinated, and/or fluorinated solvents, and
● Solvent suppression homo-decoupling sequences for hydrogen containing solvents.[8]

The use of smaller scale analytical columns and lower injection volumes (25 to 100µL) has drastically reduced the total solvent needed (20 to 30mL) for the LC-^{1}H NMR experiment. This has helped to greatly reduce costs when relatively expensive deuterated solvents must be used. The LC-^{1}H NMR technique, utilized as a quantitative analytical tool, was first reported in 1982.[5]

SECTION II. INTRODUCTION

As stated earlier, this research was initiated to support the Army's capability to identify the components of fuels which contribute to low temperature performance of fuels. It is essential not only for research and development efforts within this Center, but in the continuation of cooperative programs with Project Managers of vehicles, equipment, and weapon systems, such as the Abrams tank and PATRIOT, for solving low temperature operational problems. In addition to determining the effects of diesel fuel components that contribute to low temperature inoperability, the purpose of the research was expanded to include attempting to elucidate the effects of the concentration of various chemical species or classes of compounds in middle distillate fuels on the chemical, physical, and performance characteristics of these fuels. Examples of these chemical species are: alkanes, monocyclic aromatics, dicyclic aromatics, fluorenes, and phenanthrenes. With the prediction of the deterioration in the quality of diesel fuels in the future, which is well documented in the literature, it is imperative that the effects of these chemical species on operability, which can be related to physical properties—such as cloud point, viscosity, cetane number—be fully understood. It has been seen in the field that the quality of fuels can have serious consequences on DOD's mission by degrading vehicles, equipment, and weapon systems performance and damaging critical vehicles, equipment, and weapons components. DOD's highest priority goal in mobility fuels technology is to achieve the capability of utilizing fuels which are now readily available and are projected to be available from the commercial sector. This is essential because DOD's mission cannot be unduly influenced by short-term fluctuations in petroleum supplies. Therefore, it is mandatory that all factors influencing operability be understood.

Although this research was initiated because of cold weather operability problems in vehicles and equipment, it was discovered that various physical properties of middle distillate fuels, including the cloud point, can be predicted. The LC-^{1}H NMR technique developed can predict the following physical properties:

- Cetane number (ASTM D613)
- Cetane index (ASTM D976)
- Density (ASTM D1298)
- Specific gravity (ASTM D1298)
- Pour point (ASTM D97)
- Flash point (ASTM D93)
- Viscosity (ASTM D445)
- Filterability (ASTM D4539)
- Heat of combustion (ASTM D240)
- Cloud point (ASTM D2500)
- Volume percent aromatics (ASTM D1319)
- Residual carbon content (ASTM D524)
- Initial, 10%, 50%, 90% and end boiling points (ASTM D86).

4

It was also discovered that this technique provides chemical insight concerning the influence of chemical changes on the fuel's physical properties. This led to expansion of the initial research goal. Therefore, the revised goal was to develop a simple analytical technique which can be used to rapidly predict various physical properties of fuels.

The LC-^{1}H NMR technique is now being developed to predict various physical properties of middle distillate fuels based on a single analytical technique. This methodology determines the average molecular composition data of the monocyclic and dicyclic aromatic, fluorene, and phenanthrene fractions. It also determines the fraction of total carbon for the alkane fraction. Finally, it determines, where applicable, the fraction of total carbon for the tricyclic or aromatic fraction. The on-line LC-^{1}H NMR data is also analyzed to give the following results: the molar quantities of each type of hydrogen and carbon present in the fuel samples, an average structure for each chemical class, and an average molecular structure for each class. A complete description of this average molecular approach has been published.[6] Also, the ^{1}H and ^{13}C NMR analysis provides aromaticity data.

Once the LC-^{1}H NMR and[13]C NMR data is collected and analyzed, the process of predicting physical properties begins. This is the process of determining the relationship between chemical structures (alkanes, monocyclic aromatics, and dicyclic aromatics) and physical properties (cloud point, density, and cetane number). The prediction of properties is approached from a "group property" point of view. This group property approach of using chemical properties to calculate physical properties of classes of compounds has been utilized by chemists for several years. In the group property approach, the structure of the molecule is examined for structural features which dictate the physical properties of the compounds. In other words, the physical properties of a molecule or compound are determined by the number of types of chemical groups present—methyl, methylene, methine, etc. Although synergistic effects between the chemical compounds present in a fuel could be important for some physical properties, it has been shown that a group property approach is effective in the calculation of several physical properties of pure compounds.[9] The group property approach has also been used in the calculation of physical properties of fuel mixtures.[10]

The ASTM has developed standards for fuel property analysis. These ASTM methods are recognized worldwide as being very accurate but may be tedious, as well as requiring large quantities of fuel sample. As a result, several alternatives to ASTM methods have been proposed to predict fuel properties in a more timely manner, i.e., measurement of cloud point by Differential Scanning Calorimetry[11] and an alternative to the ASTM engine test for the determination of cetane number.[12] There have also been efforts to measure only selected fuel properties and from these properties predict other physical properties of the fuel.[13]

In this research, nuclear magnetic resonance spectroscopy was developed as a liquid chromatographic detector. The LC-^{1}H NMR approach was used in the chemical fingerprinting of

middle distillate fuel samples. In this report, 17 physical properties of middle distillate fuels based on average molecular structure obtained by LC-^{1}H NMR analysis are reported. The predictions are based on the group property approach. A general predictive equation, based on the average molecular properties of each class of compounds present in the fuels, was developed. These LC-^{1}H NMR predicted property measurements were compared to measurements obtained by the ASTM fuel tests. Most measurements were found to be within experimental error.

SECTION III. RESULTS AND DISCUSSION

For several years, there has been interest in the various applications of NMR of flowing systems.[14] The interest has primarily been in the use of NMR as an on-line, continuous flow HPLC detector.[15] In this research, the NMR was used as an on-line, continuous flow HPLC detector (LC-^{1}H NMR) in the analysis of middle distillate fuel samples.

For the purpose of this research, the average composition of a low boiling fuel sample is defined in the following manner. For each hydrocarbon class, the absolute moles of each distinct carbon type (with associated hydrogens) in a specified aliquot are determined. Examples of distinct carbon types are:

- An unsubstituted aromatic ring carbon (which has one associated hydrogen), and
- Substituted aromatic ring carbon (having no associated hydrogen).

It can be seen that each of these clearly constitute a separate type of carbon. After determining the number of moles of each carbon type in a fuel aliquot, it may be possible to normalize these data to propose a hypothetical average molecular structure. Although the average structures, as defined by this research, have no real significance themselves (because they are hypothetical constructs of the normalized compositional data), quantities derived from the average structure (for example, average molecular weight) can be valuable. The major average compositional quantities discussed in this report are defined in Figure 1 (Note: All figures are contained in Appendix A.)

The research correlating fuel properties and LC-^{1}H NMR data has been divided into two parts: computer modeling of pure compounds and LC-^{1}H NMR data collection of middle distillate fuel samples.

COMPUTER MODELING OF PURE COMPOUNDS

In attempting to predict physical properties of middle distillate fuels, the initial studies concentrated on predicting the physical properties of pure compounds. This was done to gain insight regarding structure-physical property relationships. The prediction of properties was approached from a "group property" point of view. This means that the structure of a molecule is examined for

structural features which dictate the physical properties of the compounds. The group property approach is based on the following equation:

$$\text{Pure Compound Property} = \sum_{x} f^{x} C_{T} {}^{*}\text{Group Property}$$

where:

Property = cetane, density, etc.
x = alkane, monocyclic, dicyclic, fluorene, and phenanthrene
C_{T} = Total moles carbon for class x

While examining these pure compounds, a computer data base was generated containing approximately 80 compounds belonging to the chemical classes of alkanes, alkenes, cyclohexanes, decalines, monocyclic aromatics, naphthalenes, and tetralins. The first physical properties investigated were cetane number and density because they were readily obtainable in a group property approach. In all of the classes studied, it was determined that the dominate factors in the calculation of these properties are the chain length of the molecule and the degree of branching. In cyclic molecules, the degree of substitution on the ring is also found to be a dominate factor.

Next, formulas were developed for the classes to calculate the cetane number and density. For alkanes, the NMR integration of the methylene (CH_2) chemical shift region determines the chain length of the molecule. For the degree of branching in an alkane, the methine (CH) and quaternary (CQ) carbons were used. The degree of branching of an alkane is defined as:

$$CH + 2{*}CQ$$

because each methine group indicates one branch and each quaternary group indicates two branches. From this, the following formula for predicting the cetane number of an alkane was derived:

$$\text{Cetane Number} = 1.04 \left[44.0 + 1.97 \times CH_2 - 23.96 (CH + 2 \times {*}CQ) \right] - 2.38$$

This indicates that the cetane number of a base alkane is approximately 44.

Also, as the chain length increases in the molecule, the cetane number of the compound increases by approximately five for each CH_2 group. The previous formula also indicates that the cetane number decreases by approximately 25 units for each branch on the molecule.

Similar formulas were developed by multiple regression analysis for each of the previously listed compound or chemical classes. The correlation coefficients for these predictions are listed in Table 1.

7

Table 1. Correlation Coefficients of Predicted vs. Observed Values for Cetane Number and Density of Compounds or Chemical Classes

COMPOUND CLASS	CETAINE NUMBER CORRELATION	DENSITY CORRELATION
Alkanes	0.927	0.920
Alkenes	0.858	0.997
Cyclohexanes	0.979	0.896
Decalins	0.973	0.987
Monocyclics	0.952	0.865
Dicyclics	0.911	0.907
Tetralins	0.911	0.999

Finally, the cetane number was predicted for a total of 73 compounds. As shown in Figure 2, the correlation coefficient was 0.9706.

The process was repeated for the prediction of density for each of the compounds in the basic set. The same structural parameters were found to be important in determining the density of each compound as in determining the cetane number. The following formula is used for predicting the density for an alkane:

$$Density = 1.02[0.67 + 0.0033 \times CH_2 + 0.0023 \times (CH + 2 X * CQ)] - 0.139$$

The results of the compound classes are listed in Table 1. The density was predicted for a total of 63 compounds. Shown in Figure 3 is the plot of predicted versus observed density values which resulted in a correlation coefficient of 0.988.

The process was repeated to predict additional physical properties. Once the appropriate equation for each property was determined, the predicted values were plotted versus the observed values. Then the correlation coefficients shown in Table 2 were derived.

Table 2. Correlation Coefficients of Physical Properties of Pure Compounds

PROPERTY	CORRELATION COEFFICIENT	NUMBER OF POINTS*
Boiling Point	0.990039	270
Freeze Point	0.855456	154
Flash Point	0.994939	10
Refractive Index	0.993173	274
Specific Dispersion	0.988314	172
Surface Tesnion	0.962658	85
Critical Pressure	0.969109	86
Critical Temperature	0.987930	82
Critical Volume	0.988845	86
Heat Capacity	0.992611	166
Heat of Vaporization	0.995345	108
Heat of Formation	0.997171	159
Free Energy of Formation	0.998243	47
Heat of Combustion	0.999953	157

*Number of points on each plot (predicted vs. observed values); each point represents one compound.

LC-^{1}H NMR DATA COLLECTION OF MIDDLE DISTILLATE FUEL SAMPLES

A total of 109 middle distillate fuel samples (commercial fuels) were received from Belvoir Fuels and Lubricants Research Facility, Southwest Research Institute, San Antonio, TX. The samples, obtained from an industry survey program, were analyzed using continuous flow LC-^{1}H NMR, as well as static ^{1}H and ^{13}C fourier transform (FT) NMR techniques. The following data was collected for each sample:

- Average molecule composition data for the monocyclic and dicyclic aromatic fractions ($*C^m_{un}$, $*C^d_{un}$, $*C^m_{\alpha CH_3}$, $*C^d_{\alpha CH_3}$, MW^m)

- Static ^{1}H and ^{13}C NMR aromaticity data

- The fraction of total carbon for the alkane fraction (F^a_{total})

- The fraction of total carbon for the tricyclic or aromatic fraction, where applicable.

9

An example of the data collected for each sample is shown in Appendix B. From the above data, the following properties were derived for each fuel sample:

- Average molecular composition data for each chromatographic fraction

- Molar amounts of each component

- Average molecular properties for a given class or carbon type present through integration.

From this data, the predictive equation (Equation 1, Figure 4) was developed for various fuel properties. The equation is based on the average molecular properties of each class of compounds present in the fuel. A detailed explanation of the development of this predictive equation is included in Section IV of this report.

At this time, the actual predictions of physical properties of middle distillate fuels began. First, the property of each class of the fuel was predicted using average structural data obtained by LC-NMR analysis of the fuel. After the properties of the individual classes were determined, the property of the fuel was calculated by taking a weighted average of the properties of each class. The weighing factor consisted of the fraction of carbon in the fuel which was present in each individual class.

Using Equation 1 (Figure 4), 17 physical properties of the 109 fuel samples were predicted from the LC-^{1}H NMR data. Table 3 summarizes the results. Although there was a total of 109 fuels in the data base, values for all measured physical properties were not available for each of the fuels. However, the maximum number of fuels for which the ASTM physical property data were available was included in each correlation. The correlation plots (observed vs. calculated values) for the 17 physical properties are shown in Figures 5 through 21.

Table 3. Summary of Fuel Physical Property Predictions

PROPERTY	r*	N**	n***	RANGE OF VALUES	UNITS
Cetane Number	0.9672	30	1	38 to 48	Cetane
Cetane Index	0.9789	65	1	37 to 57	Cetane
Density	0.9653	64	1	0.791 to 0.891	kg/L
Specific Gravity	0.9731	37	1	0.825 to 0.870	60/60°F
Initial Boiling Point	0.8995	64	–1	151 to 220	°C
Boiling Point: 10%	0.9393	67	–1	170 to 252	°C
Boiling Point: 50%	0.9532	104	–1	193 to 301	°C
Boiling Point: 90%	0.9185	105	–1	224 to 373	°C
End Boiling Point	0.9142	102	–1	244 to 406	°C
Pour Point	0.9080	72	1	–43 to 10	°C
Flash Point	0.7129	103	1	36 to 83	°C
Cloud Point	0.9284	70	1	–29 to 14	°C
Viscosity	0.9517	104	1	1.1 to 4.3	cSt
Filterability	0.7970	38	1	9 to 78	
Heat of Combustion	0.9298	29	1	42.7 to 43.2	MJ/kg
Percent Aromatics	0.9733	70	1	14.8 to 42.1	vol %
Residual Carbon	0.8137	83	1	0.09 to 2	vol %

*r = correlation coefficient

**N = number of points (fuels)

***n = function type exponent

Next, errors of each property prediction by the LC-^{1}H NMR technique were determined. The error of the physical property prediction was given as the standard deviation of the residuals (σ_r) from the prediction. These values were compared to the reproducibility values of the ASTM methods for determining each fuel property. The errors of each physical property prediction and the reproducibility of the ASTM methods are summarized in Table 4. It can be seen from this table that most of the LC-^{1}H NMR predictions are within the experimental error of the ASTM measurement for that property.

Table 4. Comparison of ASTM Quoted Errors and LC–^{1}H NMR Method Standard Deviation of Residuals

PROPERTY	ASTM METHODS	ASTM* REPEATABILITY	ASTM* REPRODUCIBILITY	CALCULATED σ_r	UNITS
Cetane Number	D613	0.7	2.9	0.85	Cetane
Cetane Index**	D976	2.0		1.10	Cetane
Density	D1298	0.0005	0.0012	0.005	kg/L
Specific Gravity	D1298	0.0005	0.0012	0.002	60/60°F
Initial Boiling Point	D86	2	5	5.88	°C
Boiling Point: 10%	D86	2	5	6.25	°C
Boiling Point: 50%	D86	2	5	9.91	°C
Boiling Point: 90%	D86	2	5	18.8	°C
End Boiling Point	D86	2	5	20.6	°C
Pour Point	D97	3	6	5.18	°C
Flash Point	D93	5	10	9.47	°C
Cloud Point	D2500	2	4	3.77	°C
Viscosity	D445	0.05	0.24	0.27	cSt
Filterability***				19.1	
Heat of Combustion	D240	0.13	0.40	0.06	MJ/kg
Percent Aromatics	D1319	1.4	3.0	1.85	vol %
Residual Carbon	D524	0.16	0.26	0.29	vol %

* The exact reproducibility and repeatability for the ASTM tests are dependent on the fuel class being tested and the exact conditions of the test. The values presented here are representative for the fuels utilized in this tudy.

** The cetane index is a correlation with the cetane number. Therefore, the error in cetane index is dependent on the error in the cetane number. ASTM D976 quotes only the error shown here.

*** The filterability data utilized for this study was a filterability index, and not the filterability measured by ASTM D4539.

One feature of this method is that the data base compiled for the correlation of the fuel properties can include various classes of fuels. For example, Figure 7 illustrates the density predictions with the individual fuels labeled JP-5, JP-8, and DF-2. Therefore, the plot of observed versus calculated density values indicates which predicted value corresponds to a fuel contained in a specific class. As a result, the ability exists to make the determination of a fuel class of a middle distillate fuel of unknown origin based solely on the LC-^{1}H NMR predicted density. This is a possibility for all physical properties predicted by this technique.

Another feature of this method is that it is possible to directly determine the influence of each chemical group type on an individual fuel property. The comparison between the values for the product of the average molecular structure parameter, fraction carbon parameter, and mixing

coefficient, shows the relative importance of each chemical group type on the physical property being studied. Figures 22 through 38 show the distribution of these three term products in the prediction of the 17 physical properties. The bar graphs consist of 14 clusters of three bars each. Each three bar cluster represents one b_i term in Equation 1. The center bar represents the average of the three term products for each chemical group type over the entire range of fuels used in the prediction of the physical property, while the outermost bars represent the minimum and maximum values of the product based on all fuels in the particular correlation. These plots make it possible to determine which properties are dependent on chemical structure of the fuel and which properties are dominated by the b_0 (base) value.

An example of the above is illustrated in Distribution Products plots of the initial and end distillation boiling points. Figure 26 (Initial Boiling Point) shows that the initial boiling point of the fuels is relatively insensitive to the chemical composition of the fuel but is dominated by the base value. However, by examining Figure 30 (End Boiling Point) it can be seen that there is a greater dependence on the chemical structure of the fuel. Not only are the term products more important in the end boiling point, but the broad range of product values, as seen by the range between the minimum and maximum bars in each three bar cluster, indicate that the end boiling point is much more sensitive to variations in the chemical structures of the fuels. This trend can also be seen in Figures 9 and 13—the correlation plots of predicted versus observed initial and end boiling points. The plot of the initial boiling point exhibits very little distinction between the fuel classes present in the data base. However, the end boiling point plot shows large distinctions between the DF-2 fuels and the JP-5 and JP-8 fuels. The correlation plots verify the conclusions drawn from the distribution of products plots.

This method also allows for the determination of which b_i terms have a positive effect on a physical property (increase the value of the property), and which have a negative effect. This is demonstrated in the Distribution of Products plots of cetane number and cetane index (Figures 22 and 23). It should be noted that the points (fuels) are limited on these plots because of the following reasons. The correlation plot of predicted versus observed cetane number (Figure 5) contains only 30 points because it is a plot of fuels that did not contain any cetane improver. At the present time, the compounds added as cetane improvers cannot be detected by ^{1}H NMR. Therefore, their effects cannot be predicted by the LC-^{1}H NMR technique. The cetane index correlation plot (Figure 6) is limited to 65 points because that is the total number of fuels that this physical property was reported on the accompanying data sheets.

As stated earlier, it is possible to determine the influences of the fuel molecular structure(b_i terms) on the cetane number of the fuel. A review of Figures 22 and 23 reveals the same trends in both the cetane number and the cetane index. For these physical properties, an increase in the chain length of any aliphatic or aromatic fractions will increase the cetane number, whereas an increase in the

13

branching of the molecules will decrease the cetane number. For example, Figure 22 shows that the b_2 (i.e., $^aX_{CH_2}$) will increase the cetane number of the fuel. However, the b_1 and b_3 (i.e., $^aX_{CH_2}$ and $^aX_{CH_3}$) terms, which are indicators of molecular branching, both decrease the cetane number. When examining the terms in the aromatic fractions, it is revealed that b_7 and b_9 terms, which indicate the chain length of the branching, increase the cetane number of the fuel. However, examination of the b_4, b_5, and b_8 terms, which indicate the number of branches on the aromatic ring, reveals that these terms decrease the cetane number of the fuel.

The cloud point data (Figure 33) was examined to determine the effects of the b_i terms on this physical property. As revealed with the pure compounds, it was determined that the dominate factors in the calculation of this property were chain length of the molecule and the degree of branching. It can be seen that an increase in chain length of any aliphatic or aromatic fractions will increase the cloud point. This can be seen by examining the b_2 (aliphatic) and b_7 and b_9 (aromatic) terms. Further examination of the plot shows that molecular branching decreases the cloud point. This is shown in the b_1 and b_3 terms which are indicators of molecular branching. It is also shown in the b_4 and b_5 terms which indicate the number of branches on the aromatic ring. From this data, it can be seen that this method of fuel analysis provides greater insight into which molecular structures of the fuel contribute to the cloud point. Prior to this research, it could only be stated that the quantity of n-alkanes present in the fuel affected the cloud point.

Next, the data for the physical property, heat of combustion, was reviewed. The correlation plot of this property is shown in Figure 19. The correlation coefficient was determined to be only 0.9298 but this was anticipated. As can be seen in Table 3, the overall range of the heat of combustion for the fuels in the data base is only 0.50 MJ/kg. Also, as shown in Table 4, the ASTM reproducibility of the heat of combustion measurement is 0.40 MJ/kg. Therefore, the distribution of products plot (Figure 36) indicates that this physical property is almost independent of the chemical structures present in the fuel and is dominated by the b_0 value, determined by the multiple regression analysis. However, a review of the literature shows that the heat of combustion is dependent on the chemical structure of the molecule.[16] It should be noted that in the data base of the fuels for this research, no heat of combustion data was available for the DF-2 fuel samples. Therefore, only JP-5 and JP-8 fuels could be used in this prediction. These fuels are structurally similar and, more importantly, have a very narrow range of heat of combustion values. Therefore, this limited data set gives the impression that the heat of combustion of the fuels is independent of the molecular structure of the fuel. A larger data set which includes a wider range of fuel classes would probably exhibit a larger dependence on chemical structure for the determination of the heat of combustion.

The remaining predicted physical properties were examined. Reviewing the correlation plots for specific gravity (Figure 8), viscosity (Figure 17), and percent aromatics (Figure 20), shows that the LC-^{1}H NMR technique is a valid method for predicting these physical properties. However, the predictions for pour point (Figure 14), flash point (Figure 15), filterability (Figure 18), and residual carbon (Figure 21) are less satisfactory. For the latter properties, there may be a need to include

additional experimental data (enlarging the fuel data base). Also, the accuracy of the experimental measurement for some of these physical properties could be the reason for the less-than-satisfactory correlations.

The above results show that the LC-^{1}H NMR technique is a reliable method for the prediction of physical properties of middle distillate fuels. Table 4 shows a side-by-side comparison of the standard deviation of the residuals from the LC-^{1}H NMR prediction of the fuel properties and the experimental errors of the ASTM measurements of these properties. In many cases, it can be seen that it is possible to predict physical properties of the fuel by LC-^{1}H NMR analysis as accurately as by measuring the physical properties by ASTM methods. The LC-^{1}H NMR technique of the analysis has the added advantage of requiring only approximately 3 to 5 milliliters of sample, and only approximately 1 to 2 hours total analysis time, while the measurement of all 17 properties by the ASTM methods would require approximately 1 to 3 liters of fuel sample and almost 50 hours of analysis time.

SECTION IV. EXPERIMENTAL

EQUIPMENT

A Whatman Magnum-9 silica gel-PAC column was used for all liquid chromatography (LC) separations. The packing in the column was silica gel derivatized to introduce amino and cyano functionalities to the surface. Retention of aromatic hydrocarbons on this type of column was generally superior to standard silica gel columns. A special activation sequence was used to remove polar compounds. These compounds slowly bleed off with nonpolar solvents and create large background signals in the proton spectra. The following sequence of chemicals was used to remove this background: 50 mL of 10% acetonitrile-d_3 (99%-d, Aldrich) in chloroform-d (99.8%-d, Aldrich) was followed by 60 mL of chloroform-d. Then, the chromatographic solvent, 97.5% 1, 1, 1-trichlorotrifluoroethane (Freon, Miller-Stephanson Chemicals Co.) and 2.5% chloroform-d, was pumped through the column. Column equilibration was usually achieved after 60 mL of Freon/chloroform-d mixture had been pumped through the column.

There is a second source of background which is particular to semipreparative LC columns. Large internal diameter columns do not completely flush the alkane fraction because of partially stagnant regions near the inlet, outlet, and wall. This can result in a very small amount of aliphatic material being present in the spectra of the aromatic fractions of the LC-^{1}H NMR experiment. Therefore, for fuels of low aromaticity, the signal is intense enough to make an erroneously high measurement of CH_2 and CH_3 ^{1}H integrals for alkyl aromatics. The method designed to correct the column is to inject a very low aromaticity fuel and measure the relative aliphatic signal intensities in each file.

15

The chromatographic solvent contained 0.05% (v/v) hexamethyldisiloxane (HMDS, Merck) as the chemical shift and quantitation reference. The solvent was not degreased because dissolved oxygen reduces proton spin-lattice relaxation time values to several seconds.

A Waters M-45 pump was used. The pump was equipped with a needle valve to create a 1000 psi back pressure because it requires back pressure to activate its pulse dampner. A Valco injector equipped with a 100-μL sample loop was used. The sample loop was thoroughly flushed by rinsing with 1 mL of solvent followed by 1 mL of fuel sample. All fuel samples were injected neat. A guard column was used as a matter of course.

A Jeol FX-200 nuclear magnetic resonance spectrometer equipped with an Oxford 4.7-T superconducting solenoid magnet (54mm bore) was used to obtain ^{1}H spectra at 199.50 MHz. A flow cell designed for quantitative work was used for all analysis.[17] A flow probe was designed specifically for this type of analysis.[18]

A TRS-80 Model I computer was used. A floppy disk system was used for data storage. Each diskette had sufficient storage for 58 (1024 point) LC-^{1}H NMR spectra. The average composition equations were incorporated in a BASIC program.

Aromaticity was measured from ^{13}C spectra obtained at 50 MHz. To reduce ^{13}C spin-lattice relaxation times for aromaticity measurements, tris (acetyl-acetonato) chromium (III), $Cr_{(acac)_3}$, was added to each sample. Gated decoupling was for NOE suppression. To further ensure quantitative ^{13}C spectra, long pulse delays were also used. All ^{13}C spectra were run under conventional (spinning) conditions in 10-mm sample tubes.

PROCEDURES

A series of model compounds, designed to resemble typical components of diesel fuels, were made from reagent grade chemicals and were analyzed. An example of a model compound used is prepared by mixing 13.29g n-butyl-benzene, 18.47g n-petane, 10.16g m-xylene, 13.07g tetralin, 95.70g n-nonane, 56.20g hexadecane, 200.40g isooctane, 43.65g n-hexane, 85.67g dodecane, and 12.80g naphthalene. Also, 109 middle distillate fuel samples (77 DF-2, 18 JP-8, and 14 JP-5 fuels) which were supplied by Belvoir Fuels and Lubricants Research Facility at Southwest Research Institute were analyzed. All samples were subjected to on-line LC-^{1}H NMR analysis without pretreatment.

Figures 39 and 40 show block diagrams of the hardware and software of the LC-^{1}H NMR system. In the LC-^{1}H NMR approach, 100μL samples, model/pure compounds and neat fuels, were injected on a semi-prep scale normal phase chromatographic column where the samples were separated into alkane, moncyclic, and dicyclic chemical classes. These components passed through the refractive index detector. Then, the chromatographic eluent flowed directly into the superconducting NMR

magnet where ^{1}H NMR spectra were obtained on the flowing eluent stream. These ^{1}H NMR spectra were then integrated. Examples of LC and ^{1}H NMR spectra are shown in Figures 41 and 42. The approximate experimental time to obtain the LC-^{1}H NMR data was 20 to 30 minutes. From the ^{1}H NMR, the data went to the computer for analysis. The LC-^{1}H NMR data was transferred via an RS-232 serial transfer line to an IBM PS/2 Model 60 personal computer where the average structural composition data, representative of the average of all chemical structures found in each chromatographic fraction, was calculated.

The off-line ^{1}H NMR data was integrated and files containing average structure information were generated. These average molecular structure files were then compared to a set of files which contained the physical properties of each fuel determined by ASTM methods. These comparisons were made in order to establish possible correlations. These correlations between the average molecular structure data and the physical properties of the fuels were analogous to the group property predictions because the average molecular structure data provided by the LC-^{1}H NMR was a quantitative representation of the chemical groups present in the fuels.

The actual correlations were determined by multiple regression analysis of 13 LC-^{1}H NMR derived parameters and the physical properties of the fuels. The 13 LC-^{1}H NMR derived parameters characterized the chemical structure groups (Figure 43) present in the alkane, monocyclic, and dicyclic chromatographic fractions of the fuel. The multiple regression analysis provided the 14 mixing coefficients shown as b_0 - b_{13} in Equation 1 (Figure 4). **Note:** The mixing coefficients were the same for all the fuels when determining the same property, but not the same when determining different physical properties. This was the overall form for the equation produced by the multiple regression analysis. (A glossary of terms used in this equation is shown in Figure 1).

After regression coefficients were calculated, the resulting equation was for the calculation of the predicted fuel property. This equation consisted of the 13 terms derived from LC-^{1}H NMR data and the b_0 term. Actually, each of these 13 LC-^{1}H NMR terms was a product of the following three individual terms:

● The average molecular structure group contribution (e.g., $^mC^*_{UN}$)

● The mixing coefficient obtained in the multiple regression analysis (e.g., b_4)

● The fraction of total carbon contained in the respective chemical class (e.g., ^mf_c).

For example, if 30% of the total carbon in the fuel sample was contained in monocyclic aromatic molecules and, on the average, each monocyclic aromatic ring was mono substituted ($^mC^*_{UN} = 5$), the product for the $^mC^*_{UN}$ term would be ($0.3 \times 5 \times b_4$). In other words, using this approach: the b_0 terms defined a base value from which the individual molecular structures of a given fuel either increased or decreased the value for the physical property of the fuel. These molecular structures,

17

combining with the fraction of total carbon present in each class, defined the unique differences between individual fuels and therefore, dictated the physical properties of the individual fuel.

The value of the expotential n in Equation 1 was selected for a given physical property by the computer software. This allowed for the prediction of either the true fuel property or the reciprocal of the fuel property. For example, in predicting the initial boiling point, a value of n = −1 was selected and the inverse of the initial boiling point was actually predicted. The correlation was then performed, resulting in the inverted predicted initial boiling point. This value was then inverted to determine the true predicted initial boiling point, in °C. Table 3 summarized those properties predicted as an inverse function, where n = −1, and those which were predicted as a linear function, where n = 1.

SECTION V. CONCLUSIONS

The objective of this research was to develop a methodology to predict middle distillate fuel properties based on a single analytical technique (LC-^{1}H NMR). It resulted in the development of a "group property" approach to predict 17 physical properties of middle distillate fuels, i.e., DF-2, JP-8, and JP-5, from experimentally derived LC-^{1}H NMR data. In this technique, the fuel was separated into chemical classes and the average molecular structure for each class was calculated. Predictive equations based on these average molecular structures were developed to predict physical properties of the fuel samples. The physical properties which can be determined by this technique are cetane number (ASTM D613), cetane index (ASTM D976), density (ASTM D1298), specific gravity (ASTM D1298), initial, 10%, 50%, 90%, and end boiling points (ASTM D86), pour point (ASTM D97), flash point (ASTM D93), cloud point (ASTM D2500), viscosity (ASTM D445), filterability (ASTM D4539), heat of combustion (ASTM D240), percent aromatics (ASTM D1319), and residual carbon (ASTM D524).

The initial research was conducted with model/pure compounds. The pure compounds were used to gain insight regarding structure-physical property relationships. The predictions are based on a "group property" approach. This means that the structure of a molecule is first examined and then searched for structural features which dictate the physical properties of the compound. When looking at the structural formations present on the molecules, interest was particularly in structures which can be determined by NMR analysis.

While examining the pure compounds, a computer data base was generated which contained approximately 80 compounds belonging to the chemical classes of alkanes, alkenes, cyclohexanes, decalins, monocyclic aromatics, naphtahalenes, and tetralins. While developing a technique to predict physical properties, it was determined that structural features—chain length of molecule, degree of branching, degree of substitution on the ring, etc.—affected physical properties.

18

Then formulas were developed by multiple regression analysis for each compound class to predict the various physical properties—cetane number and density, etc. Once the prediction formulas were developed, correlation coefficients for predicted versus observed values can be calculated as shown in Table 3.

After completing the work with the pure compounds, research with fuel samples began. A total of 109 middle distillate fuels—77 DF-2, 18 JP-8, and 14 JP-5 fuels—were analyzed by the LC-^{1}H NMR technique. The off-line ^{1}H NMR data was integrated and files containing average structural information were generated by the computer software. This data was also analyzed by the "group property" approach. This approach was applicable because the average molecular structure data derived from the LC-^{1}H NMR was a quantitative representation of the chemical groups present in the fuels. Therefore, correlations derived between the average molecular structure data and the physical properties of the fuels were analogous to the group properties predictions.

The actual correlations derived in this research were accomplished by a multiple regression analysis of the 13 LC-^{1}H NMR-derived parameters and the physical properties of the fuel. These 13 LC-^{1}H NMR-derived parameters characterize the chemical structure groups in the chromatographic fractions in the fuels. Equation 1 (Figure 4) was the form for the equation produced by multiple regression analysis used to calculate physical properties of fuels. Once this equation was developed, correlation coefficients (shown in Table 3) were determined by the same procedures used to determine the correlation coefficients of the pure compounds. Finally, the values for physical properties calculated by the LC-^{1}H NMR were compared to values determined by ASTM methods.

This research allowed for establishment of a data base of fuel property values which can expand the research opportunities beyond predicting physical properties. Because this method has the capability to distinguish fuel classes, it also allows the direct determination of the effect that each chemical group has on an individual physical property. A comparison of the values for the product of the average molecular structure parameter, fraction carbon parameter, and mixing coefficient reveals the relative importance of each group type on the property being studied.

The insight gained by examining the chemical factors which determine each property is extremely useful in other studies. With the present predictive abilities, it is not only possible to analyze a fuel to determine the physical properties, but it would now be possible to calculate the chemical structures necessary to obtain a fuel with a desired set of physical properties. With the basic fundamental understanding of the role of molecular structure on a given physical property, it appears feasible to "tailor-make" or "tailor-design" a new fuel with the present computer algorithms. In other words, it appears possible to be able to reverse the process and calculate the required molecular compositional properties for a fuel based on input physical properties. Therefore, fuels can be blended to have specific properties ("tailor-made").

The techniques developed in this research will allow the determination of physical properties of a fuel blend before the two or more fuels have actually been mixed. The physical properties of a mixture of fuels may be calculated by calculating the structures present in a theoretical mixture of two or more fuel samples. This blending is not limited only to the mixing of fuel samples. A fuel can be blended with either a pure compound or a feedstock which allows specific tailoring of the physical properties of the resultant mixture. Using the data base of fuels developed during this research, it would be possible to build a library of available mixing feedstocks. Therefore, through a library search, it would be possible to choose the proper feedstock to achieve the desired physical properties of a given fuel blend.

The technique developed is not only limited to the fuel class, middle distillate fuels presented in this report, but it should be capable of predicting physical properties of fuels such as coal-derived liquids and fuels boiling in the gasoline range. This would require a sufficient number of these fuels, with their physical properties, to be added to the existing data base of 109 fuels. Also by establishing a data base, the opportunity exists to determine the interrelationship between the different fuel properties. For example, with middle distillate fuels, the changes in densities can be observed while observing the changes in the cetane numbers of the fuels. As a result, the relationships between all of the independent physical properties can be determined by plotting the values of one physical property against another for a series of fuels.

Finally, the LC-^{1}H NMR technique and the resulting predictive methodology could possibly have an impact in consideration of "alternate fuels" —JP-5, JP-8, etc.—for equipment powered by compression-ignition engines which specify the use of DF-2. In other words, if engine performance difficulties are experienced, the LC-^{1}H NMR approach could provide a rapid screening technique for determining potential problem areas.

This research demonstrated that the LC-^{1}H NMR approach for measuring various middle distillate fuel properties can be used as an alternative to the ASTM methods of fuel property measurement. It has been shown that it is possible to predict 17 physical properties with most of the predicted properties within the experimental error of the measurements obtained by the ASTM fuel tests. Also the LC-^{1}H NMR approach offers other advantages over the ASTM test methods. From this research, it can be seen that many physical properties can be determined in approximately 1 to 2 hours with a fuel sample approximately 3 to 5 milliliters. To determine the same properties by ASTM test methods, it would take approximately 50 hours and approximately 1 to 3 liters of fuel.

REFERENCES

1. F. J. Pass, C. Csoklish, and K. Wastl, *Proceedings of the Seventh World Petroleum Congress*, Volume III, Applications and New Uses, Part 2, p. 129 (1967).

2. *Mobil Tech Topics*, File No. 2-3, Mobil Research and Development Corporation (Issued by the Product Promotion Division of Mobil Oil Corporation).

3. "Department of Defense Liquid Hydrocarbon Fuel Policy for Equipment Design, Operation and Logistics Support," Department of Defense Directive Number 4140.43, March 11, 1988.

4. E. Bayer, K. Albert, M. Nieder, E. Grom, and T. Keller, Advances in Chromatography, (1979) 14, p. 525.

5. J. F. Haw, T. E. Glass, and H. C. Dorn, Journal of Magnetic Resonance, (1982) 49, p. 22.

6. H. C. Dorn, Analytical Chemistry, (1984), 56, p. 747A.

7. J. F. Haw, T. E. Glass, and H. C. Dorn, Journal of Magnetic Resonance, (1982) 55, p. 22.

8. E. Bayer, K. Albert, M. Nieder, E. Grom, G. Wolff, and M. Rindlisbacher, Analytical Chemistry, (1982) 54, p. 1747.

9. O. Gulder and B. Glavincevski, Ind. Eng. Chem. Prod. Res. Dev., (1986) 25(2), p. 156.

10. T. H. Defries, D. Indritz, and R. V. Kastrup, Ind. Eng. Res., (1987) 26(2), p. 188.

11. H. L. Heino, Thermochemica Acta, (1987) 114(1), p. 125.

12. S.-B. Chen, Ind. Eng. Chem. Prod. Res. Dev., (1986) 25(3), p. 392.

13. P. H. Kydd, C. J. Nowack, and S. Vining, Pre-Am. Chem. Soc. Div. Pet. Chem., (1987) 32(2), p. 545.

14. J. F. Haw, T. E. Glass, D. W. Hausler, E. Motell, and H. C. Dorn, Analytical Chemistry, (1980) 52, p. 1920.

15. J. F. Haw, T. E. Glass, and H. C. Dorn, Analytical Chemistry, (1981) 53, p. 2327.

16. S. W. Benson, *Thermal Kinetics*, Wiley, New York, (1968).

17. H. C. Dorn and D. L. Wotten, Analytical Chemistry, (1976) 48, p. 2146.

18. J. F. Haw, T. E. Glass, and H. C. Horn, Analytical Chemistry, (1981) 53, p. 2332.

APPENDIX A. LIST OF ILLUSTRATIONS

m	slope factor
B	intercept factor
f(x)	function type (ie, f(x)=X or f(x)=1/X)
$b_{0\text{-}13}$	mixing coefficients from regression analysis
$^{a}f_c$	fraction of fuel carbon contained in the alkane chromatographic fraction
$^{m}f_c$	fraction of fuel carbon contained in the monocyclic chromatographic fraction
$^{d}f_c$	fraction of fuel carbon contained in the dicyclic chromatographic fraction
$^{a}X_{CH_3}$	mole fraction of alkane methyl carbon
$^{a}X_{CH_2}$	mole fraction of alkane methylene carbon
$^{a}X_{CH}$	mole fraction of alkane methine carbon
$^{x}C^{*}_{UN}$	number of unsubstituted aromatic sites (x = monocyclic or dicyclic)
$^{x}C^{*}_{\alpha CH_3}$	number of methyl carbons α to aromatic rings (x = monocyclic or dicyclic)
$^{x}C^{*}_{\alpha CH_2}$	number of methylene carbons α to aromatic rings (x = monocyclic or dicyclic)
$^{m}C^{*}_{\alpha CH}$	number of methine carbons α to monocyclic rings
$^{m}C^{*}_{\alpha C_{tet}}$	number of tetralin carbons α to monocyclic rings
$^{x}C^{*}_{CH_2 > \alpha}$	number of methylene carbons not bonded to aromatic rings (x = monocyclic or dicyclic)

Figure 1. Definitions of average compositional quantities

Number of Points = 73
Correlation Coeff = 0.9706

■ Group Property Cetane
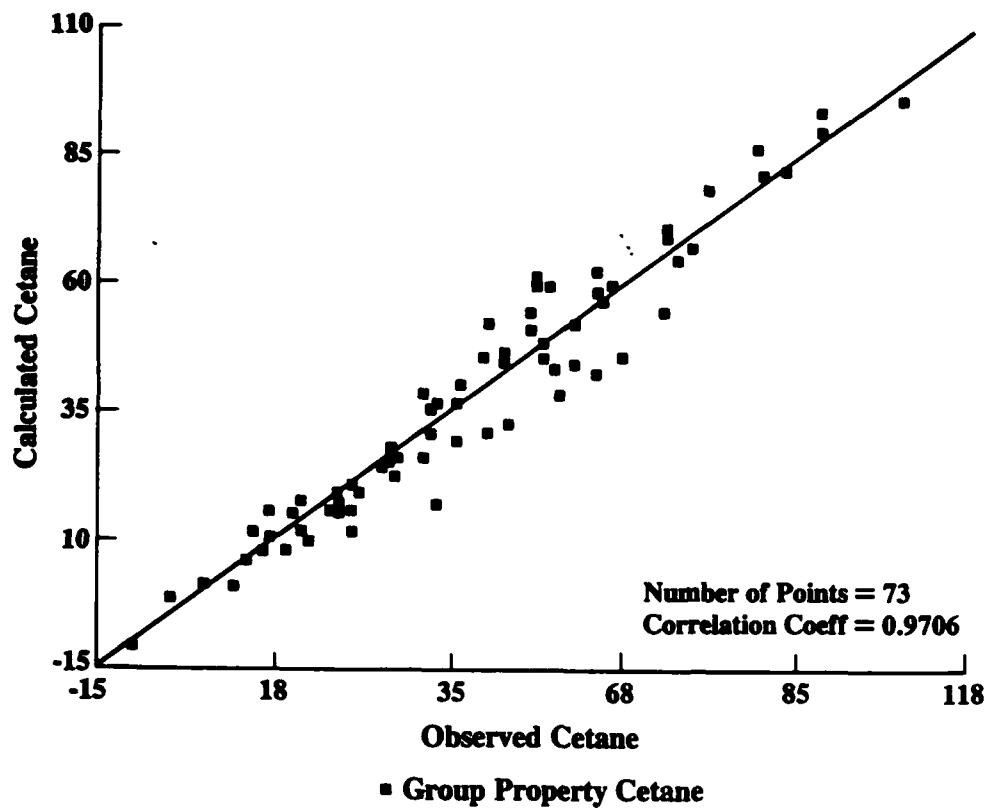
Figure 2. Correlation Plot for Cetane Number

Number of Points = 63
Correlation Coeff = 0.988

■ Avg Structure - Density
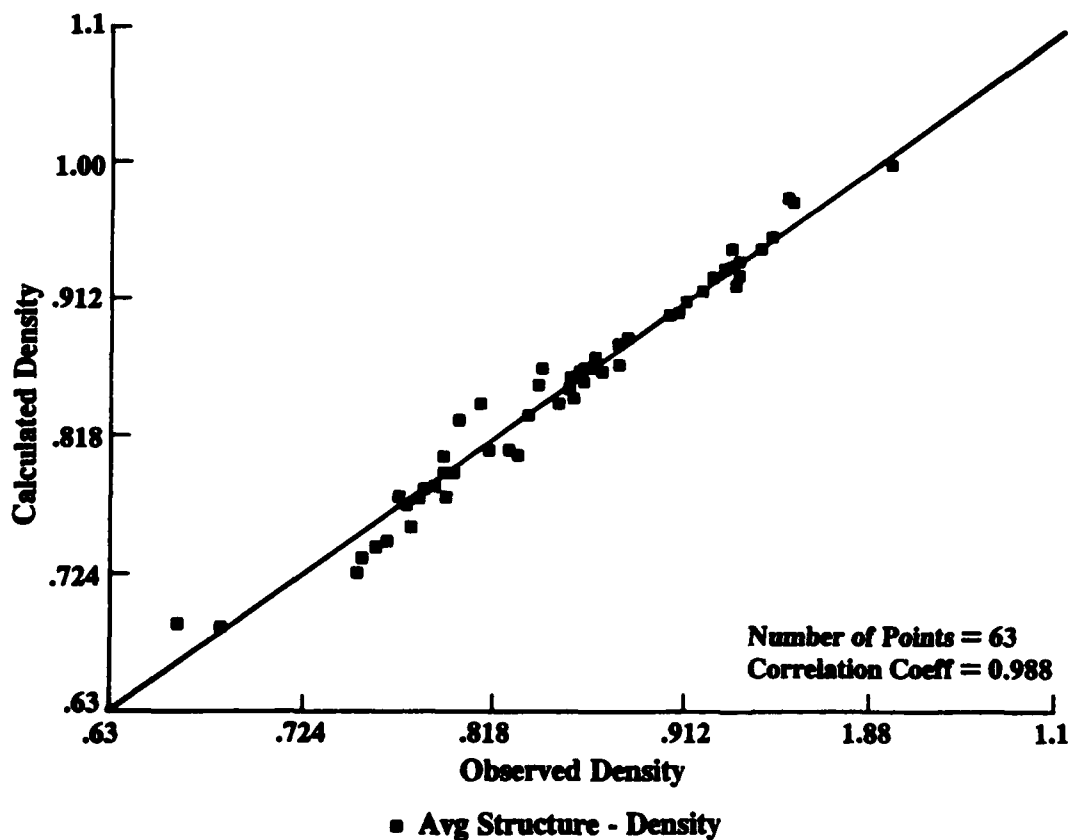
Figure 3. Correlation Plot for Density

$$\text{Property} = m * \{ b_0$$

$$+$$

$$^a f_c \left(b_1 \, {}^a X_{CH_3} + b_2 \, {}^a X_{CH_2} + b_3 \, {}^a X_{CH} \right)$$

Alkane

$$+$$

$$^m f_c \left(b_4 \, {}^m C^*_{UN} + b_5 \, {}^m C^*_{\alpha CH_3} + b_6 \, {}^m C^*_{\alpha CH_2} + b_7 \, {}^m C^*_{\alpha CH} + b_8 \, {}^m C^*_{\alpha C_{tet}} + b_9 \, {}^m C^*_{CH_2 > \alpha} \right)$$

Monocyclic

$$+$$

$$^d f_c \left(b_{10} \, {}^d C^*_{UN} + b_{11} \, {}^d C^*_{\alpha CH_3} + b_{12} \, {}^d C^*_{\alpha CH_2} + b_{13} \, {}^d C^*_{CH_2 > \alpha} \right) \}^n + B$$

Dicyclic

Figure 4. Formula for correlation of physical properties - Equation 1
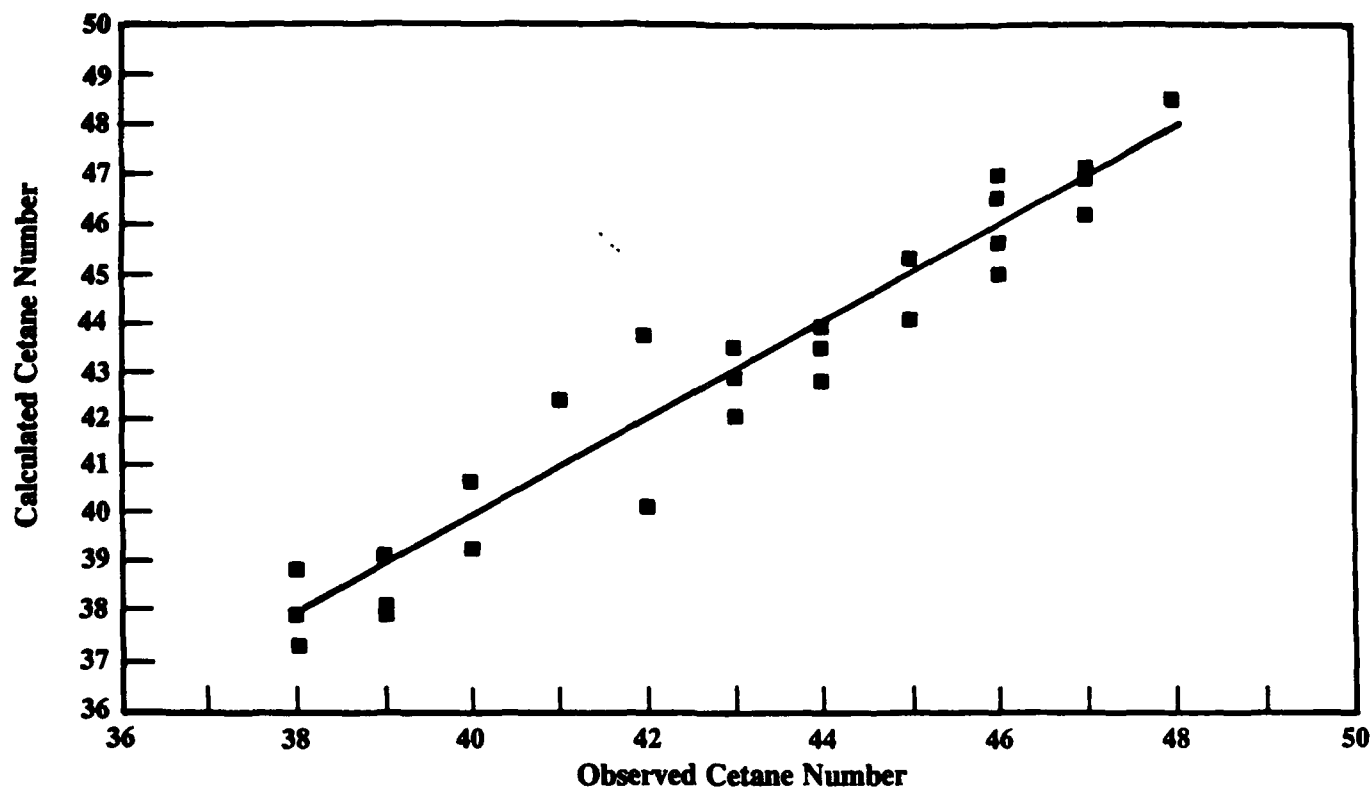
Figure 5. Correlation Plot for Cetane Number
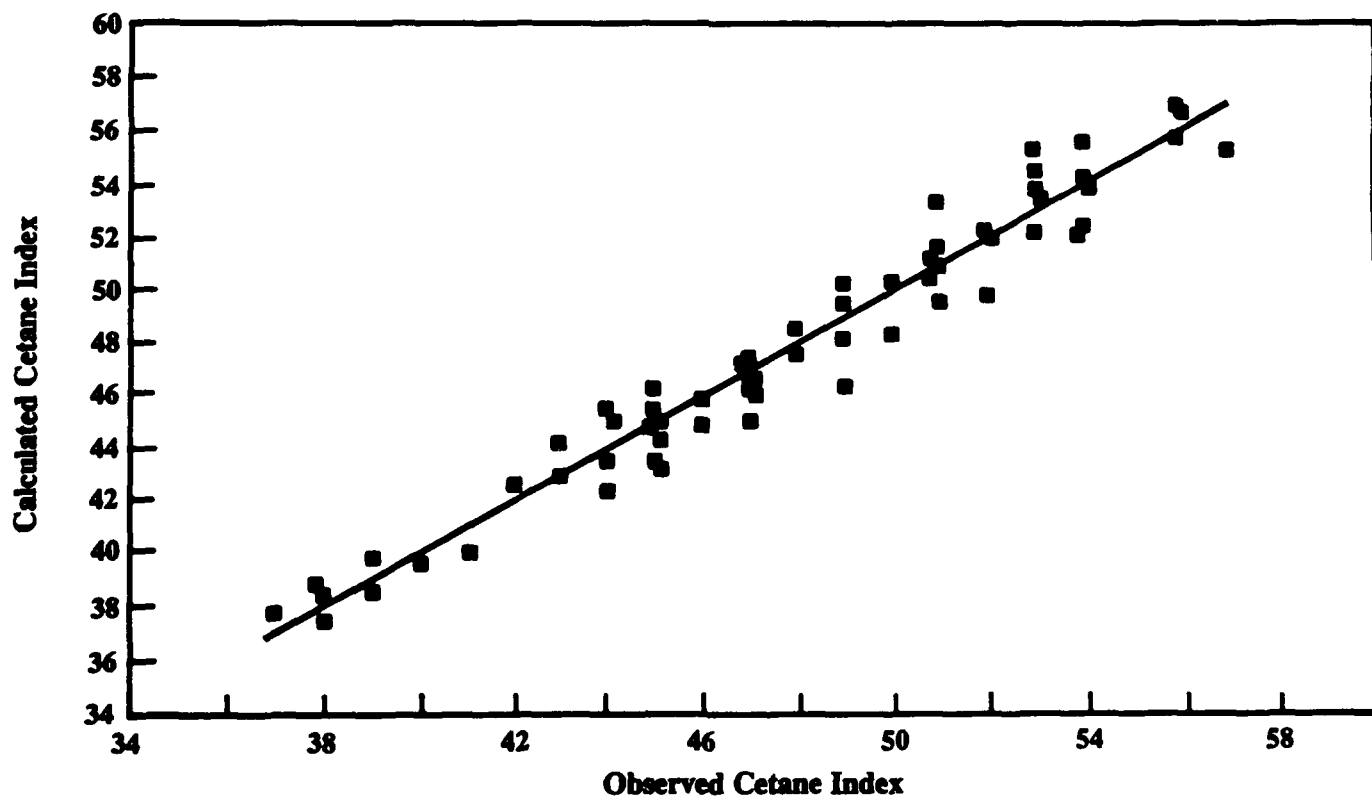
Figure 6. Correlation Plot for Cetane Index

A-5
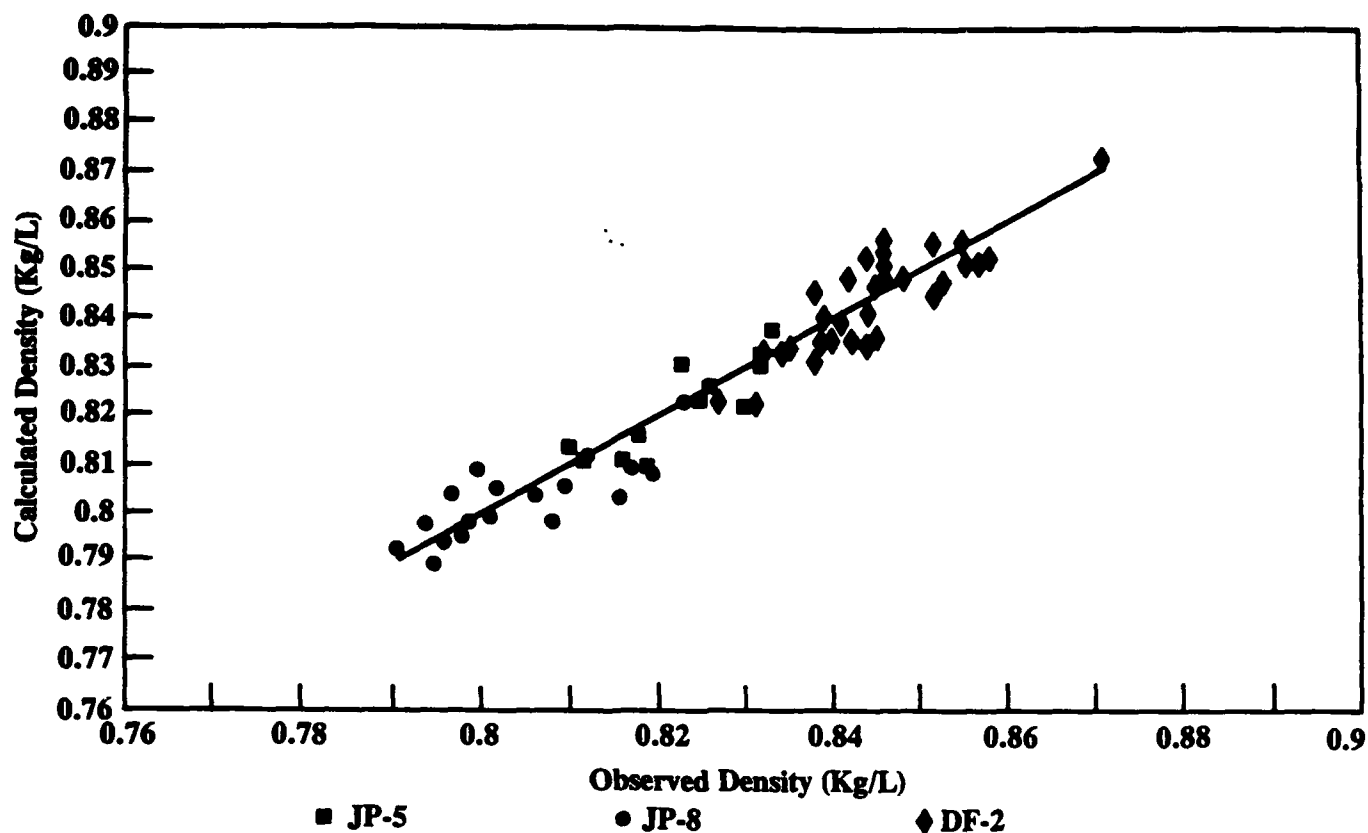
Figure 7. Correlation Plot for Density
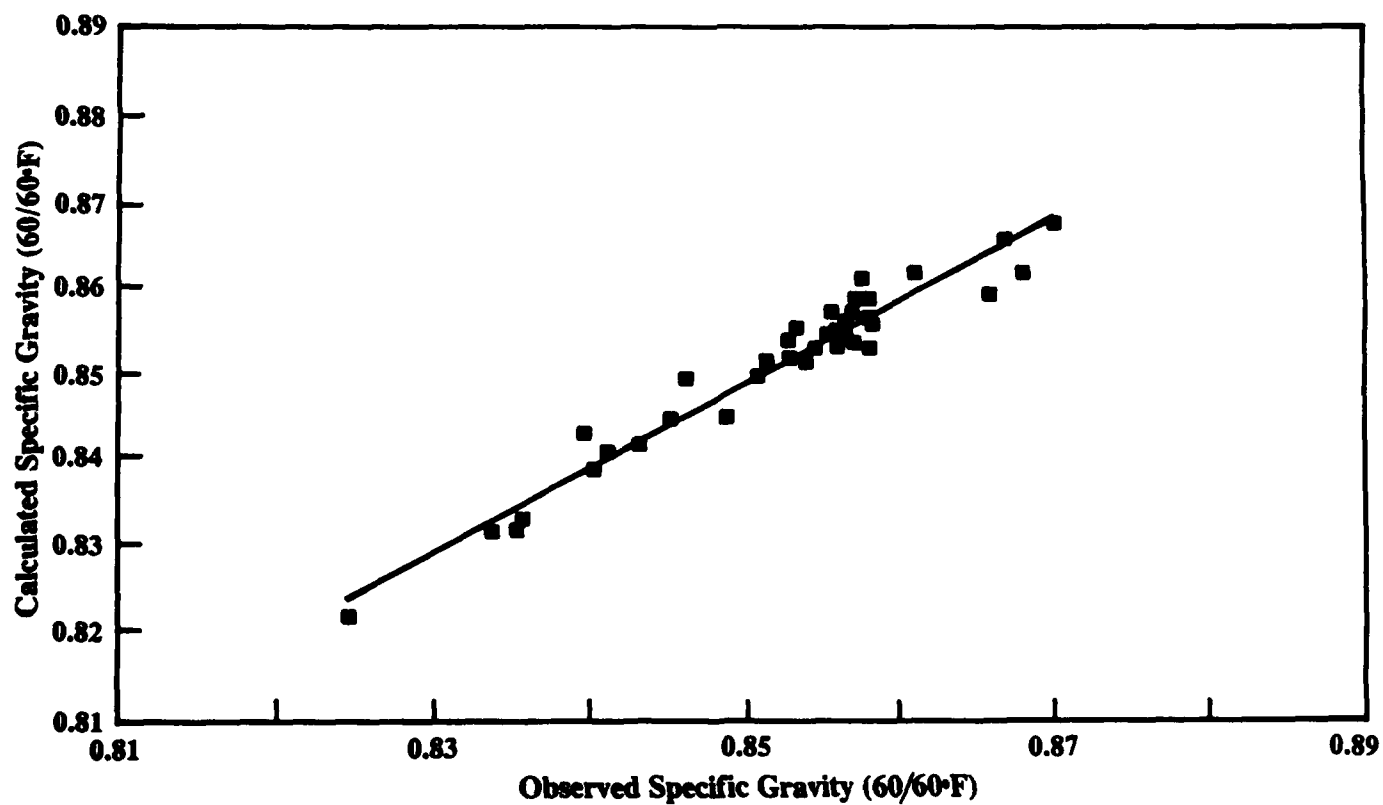
Figure 8. Correlation Plot for Specific Gravity
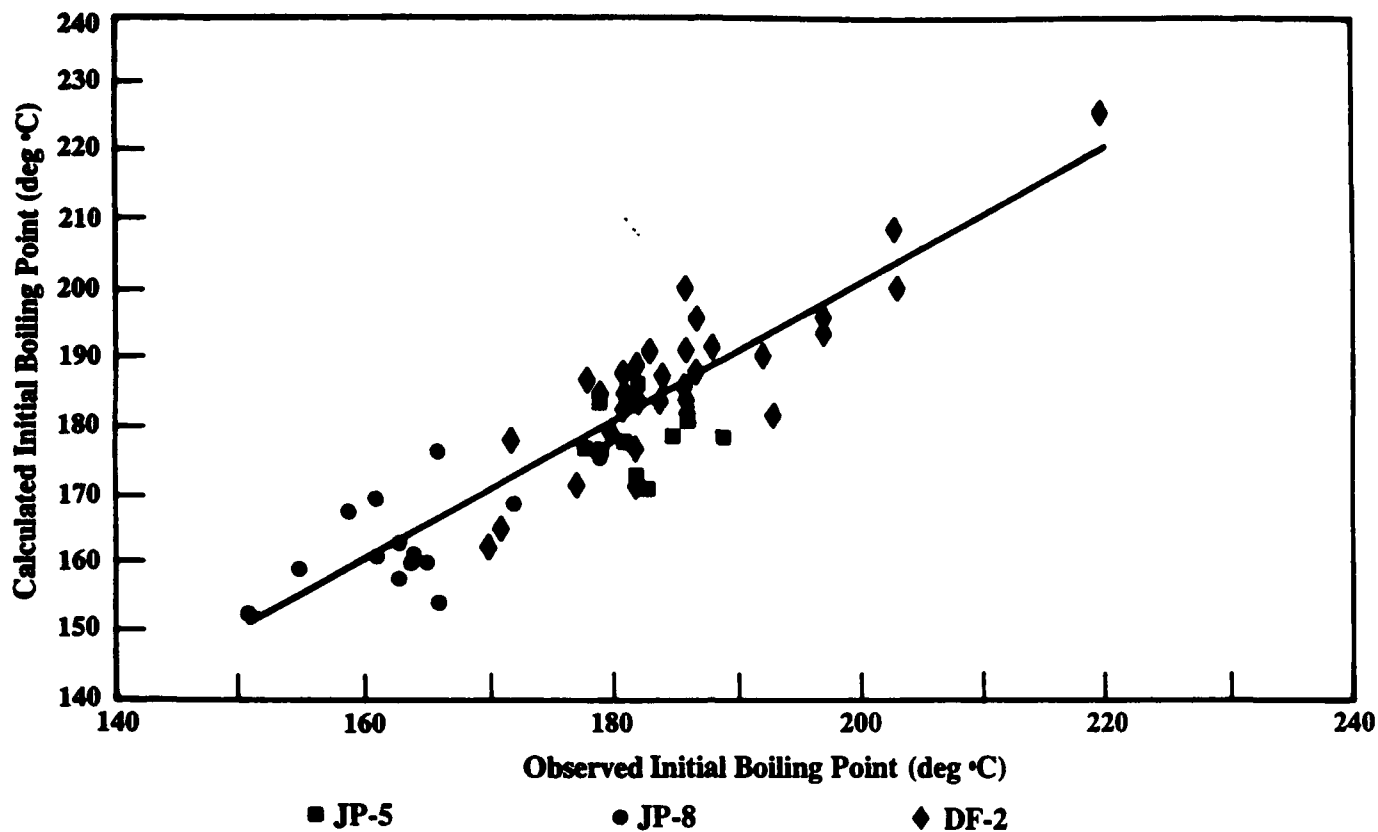
Figure 9. Correlation Plot for Initial Boiling Point
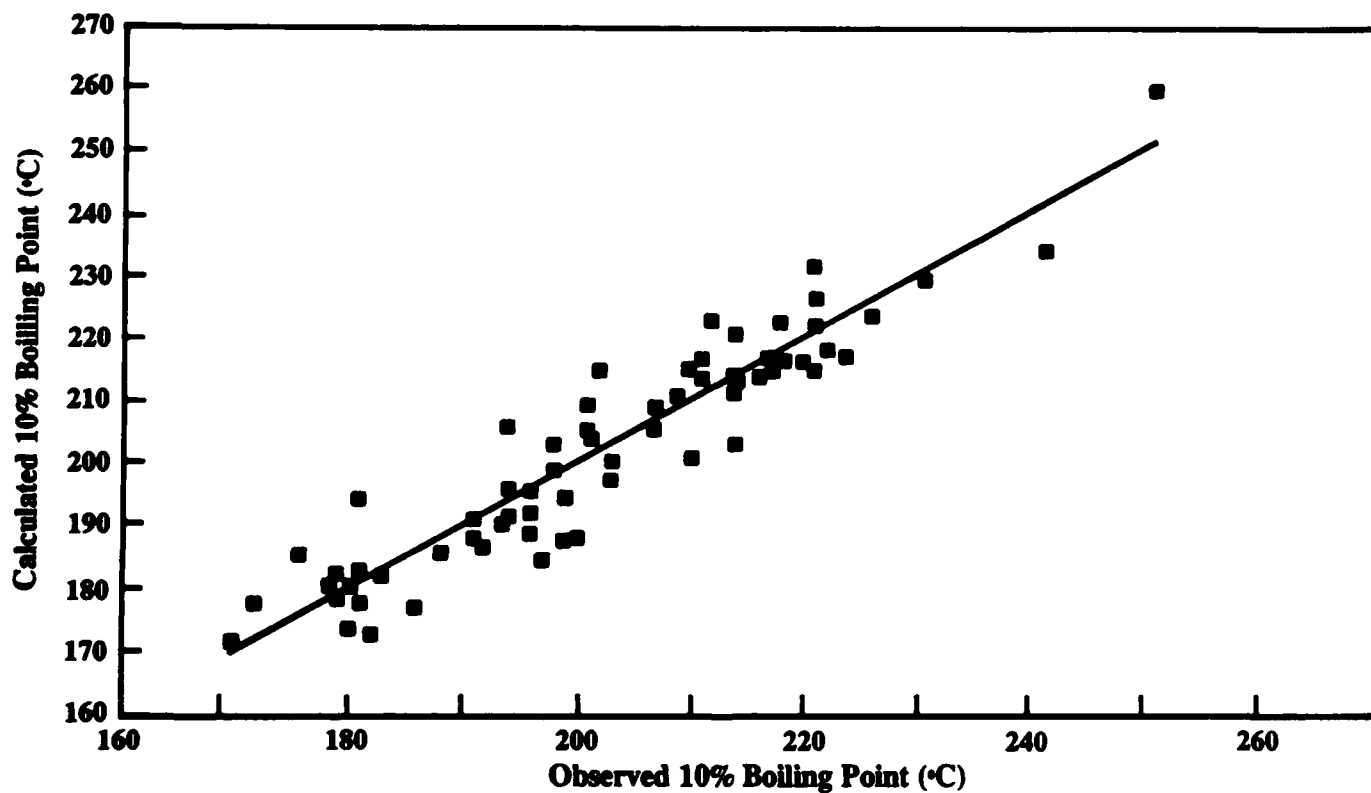
Figure 10. Correlation Plot for Boiling Point: 10%
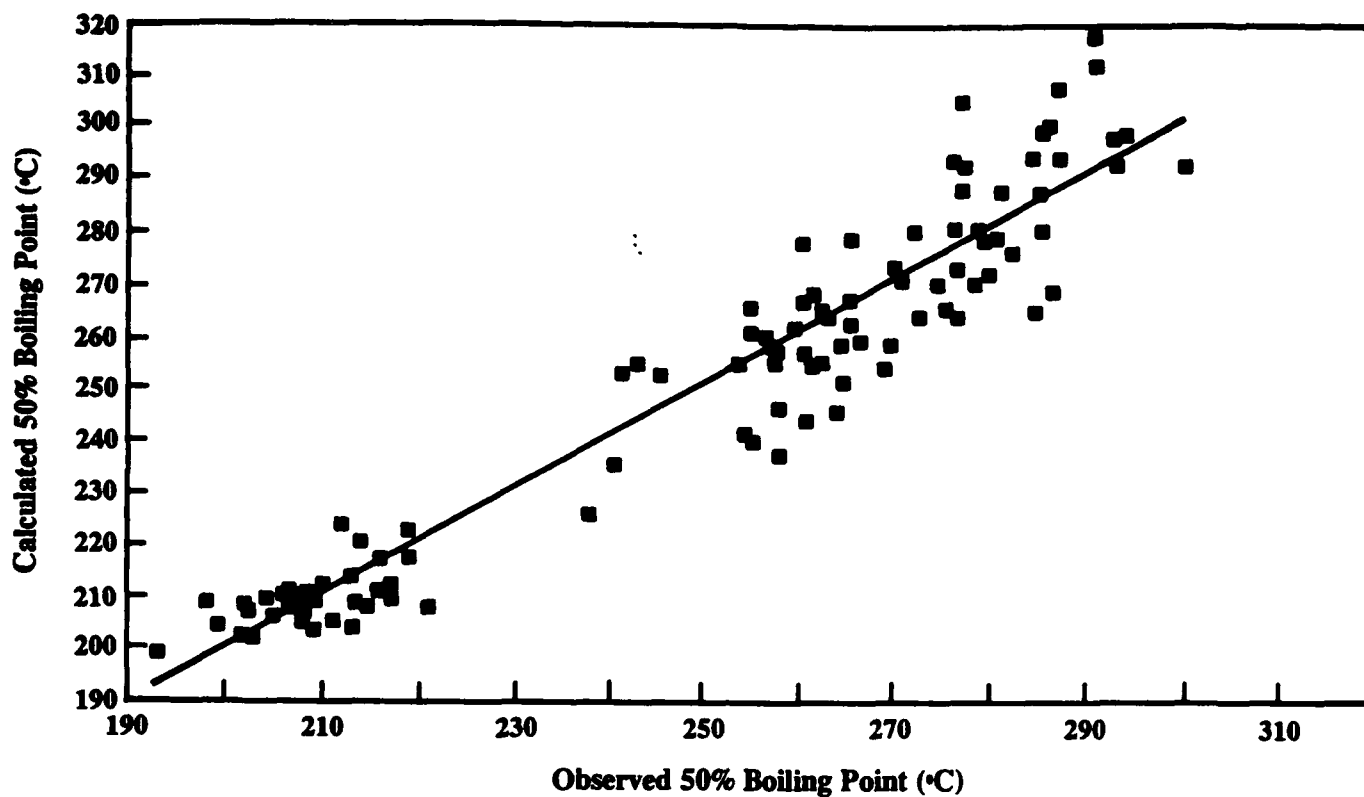
Figure 11. Correlation Plot for Boiling Point: 50%
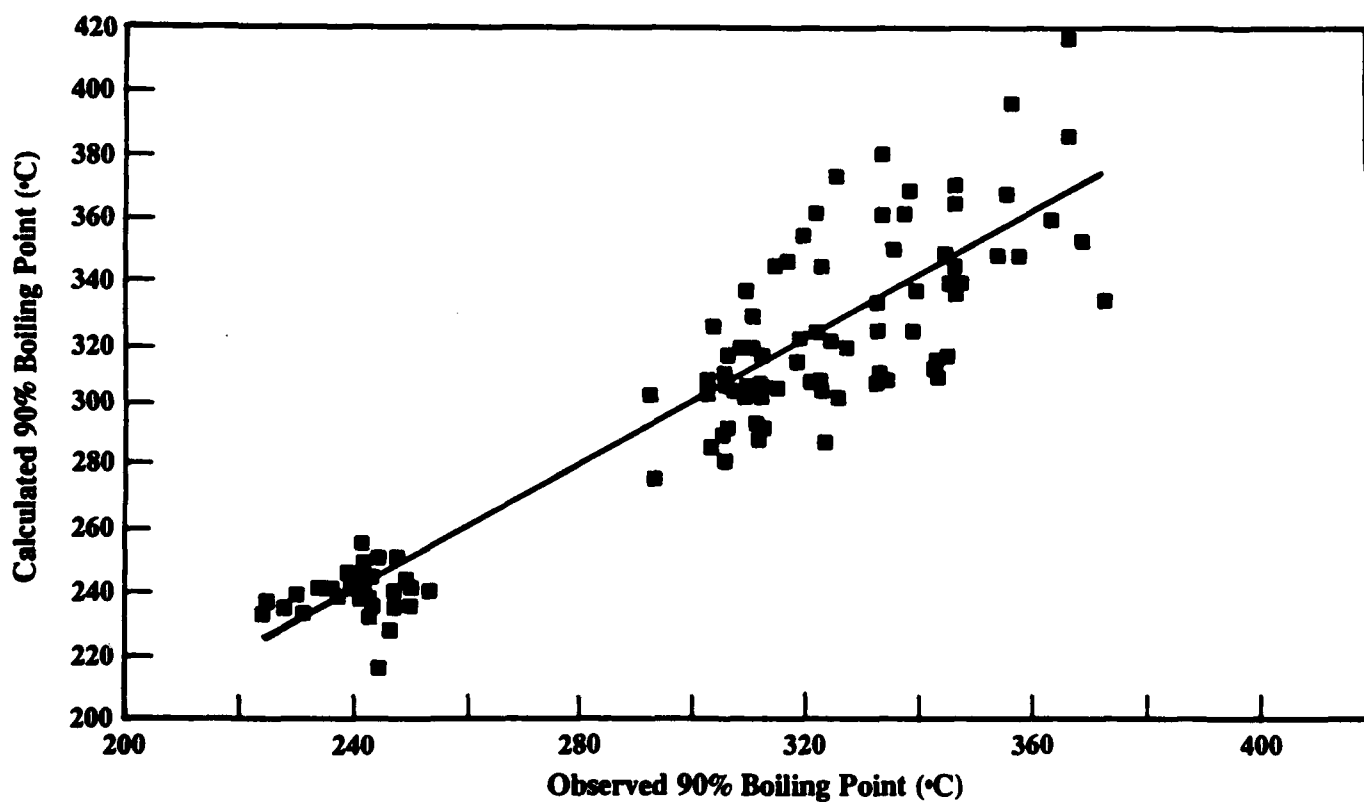
Figure 12. Correlation Plot for Boiling Point: 90%

A-8
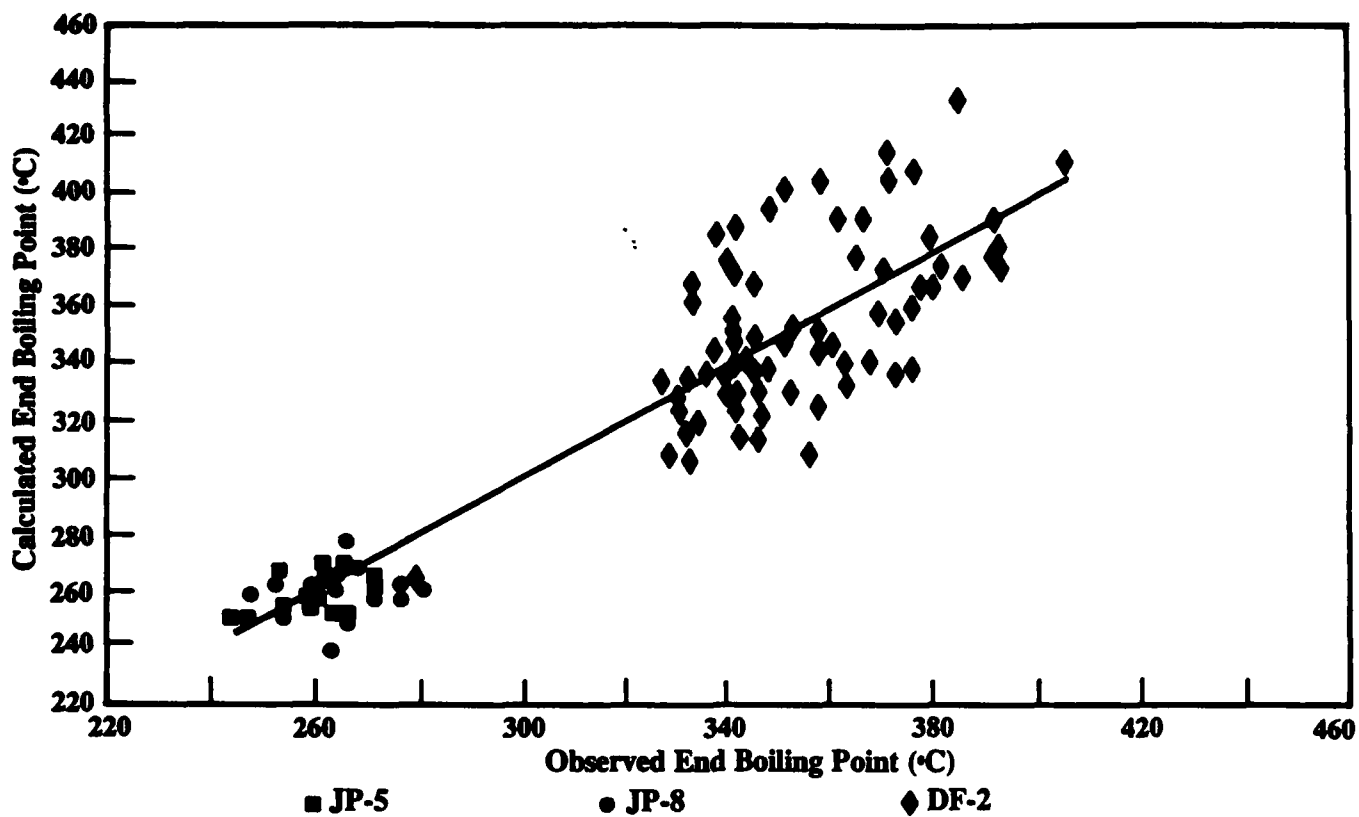
Figure 13. Correlation Plot for End Boiling Point
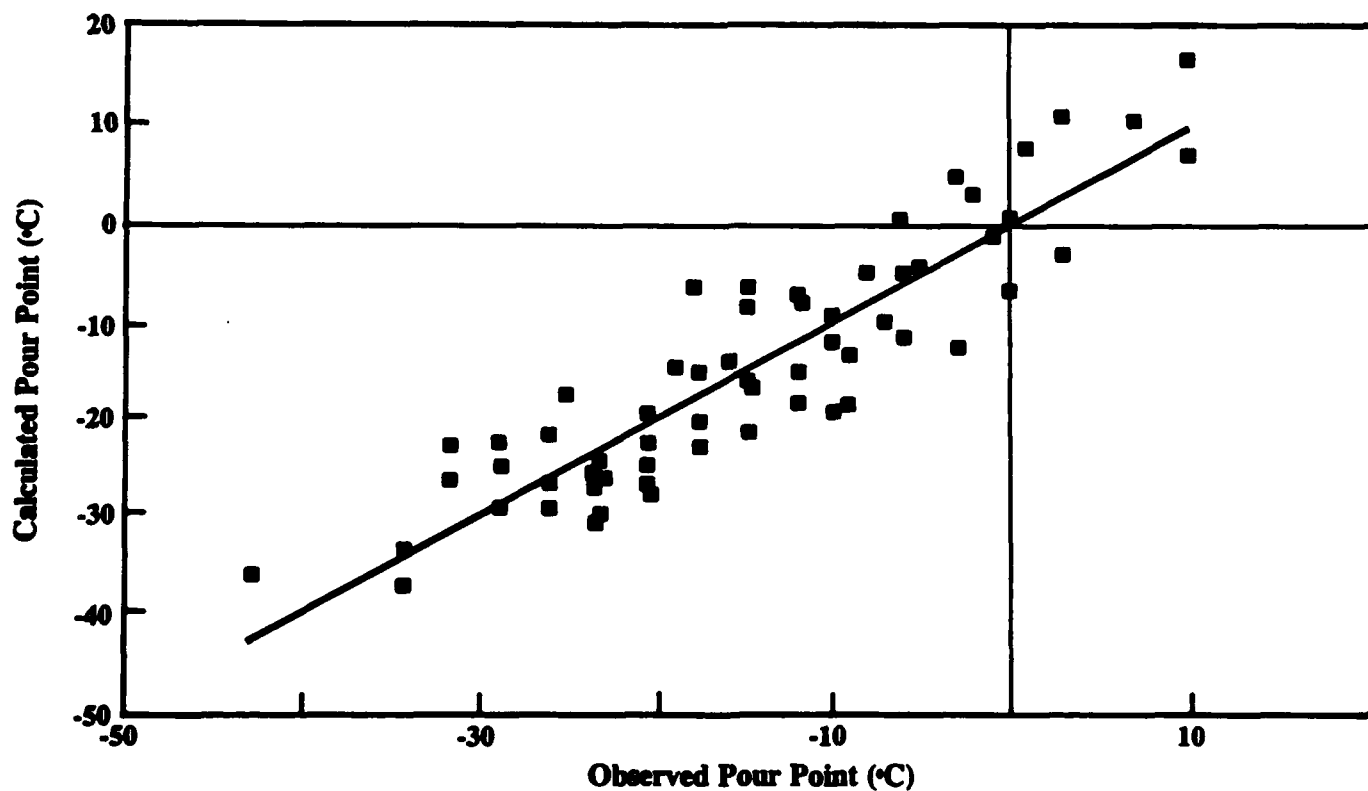
Figure 14. Correlation Plot for Pour Point
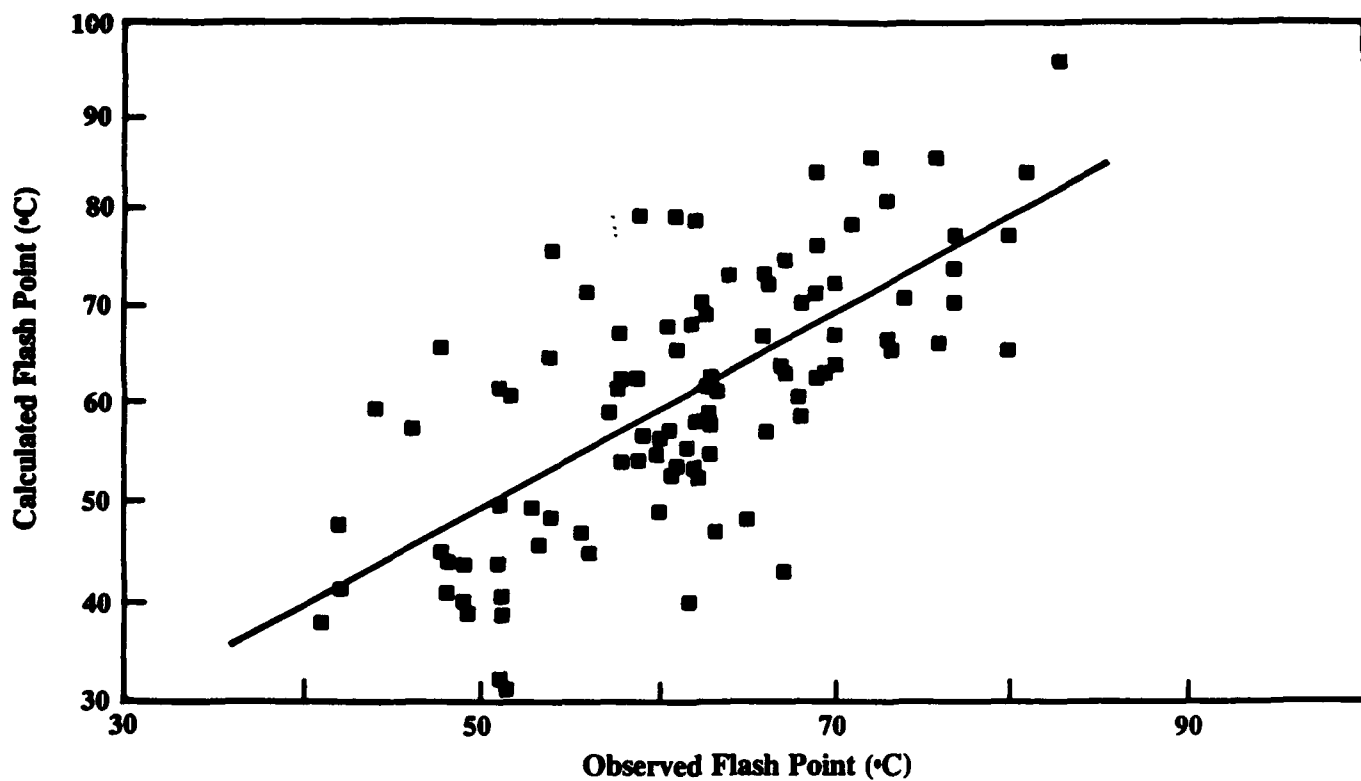
Figure 15. Correlation Plot for Flash Point
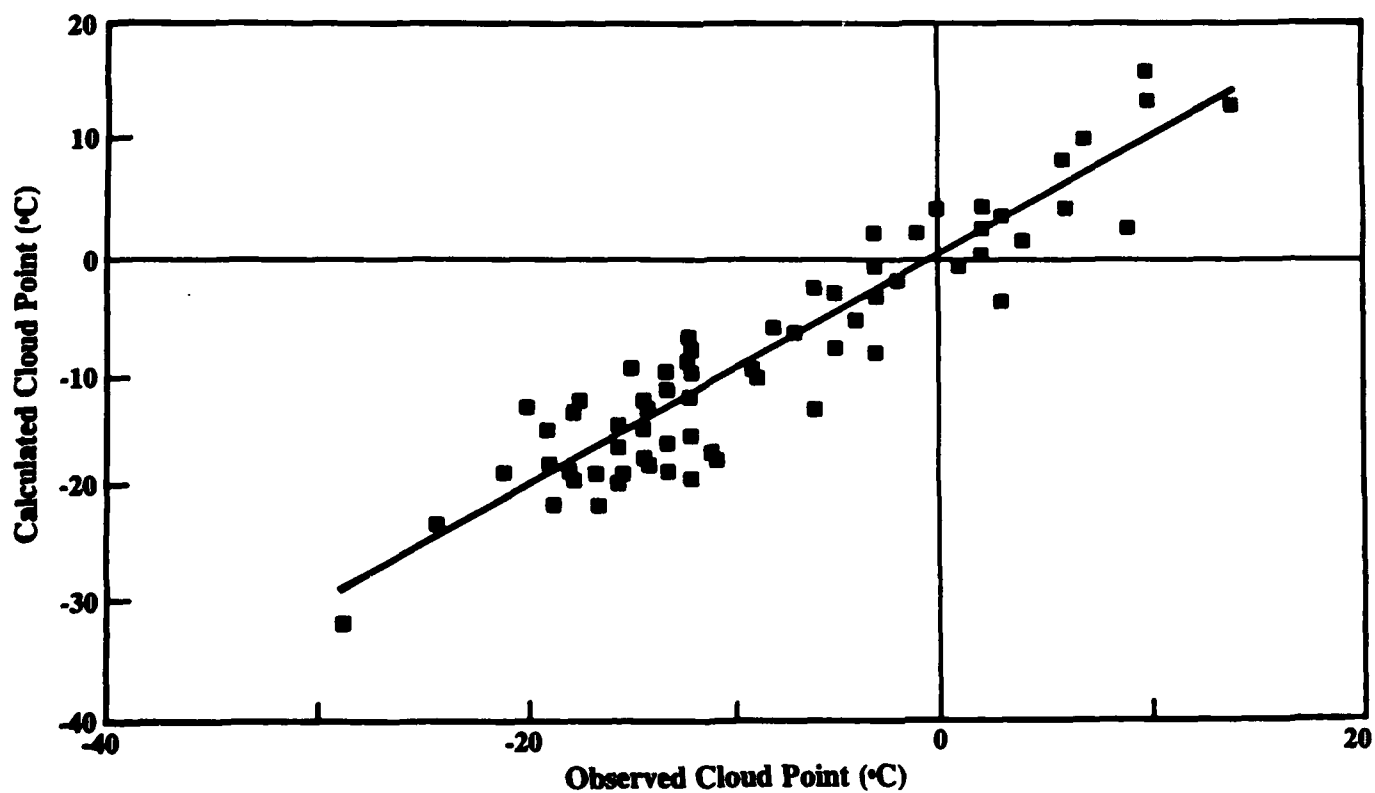
Figure 16. Correlation Plot for Cloud Point

A-10
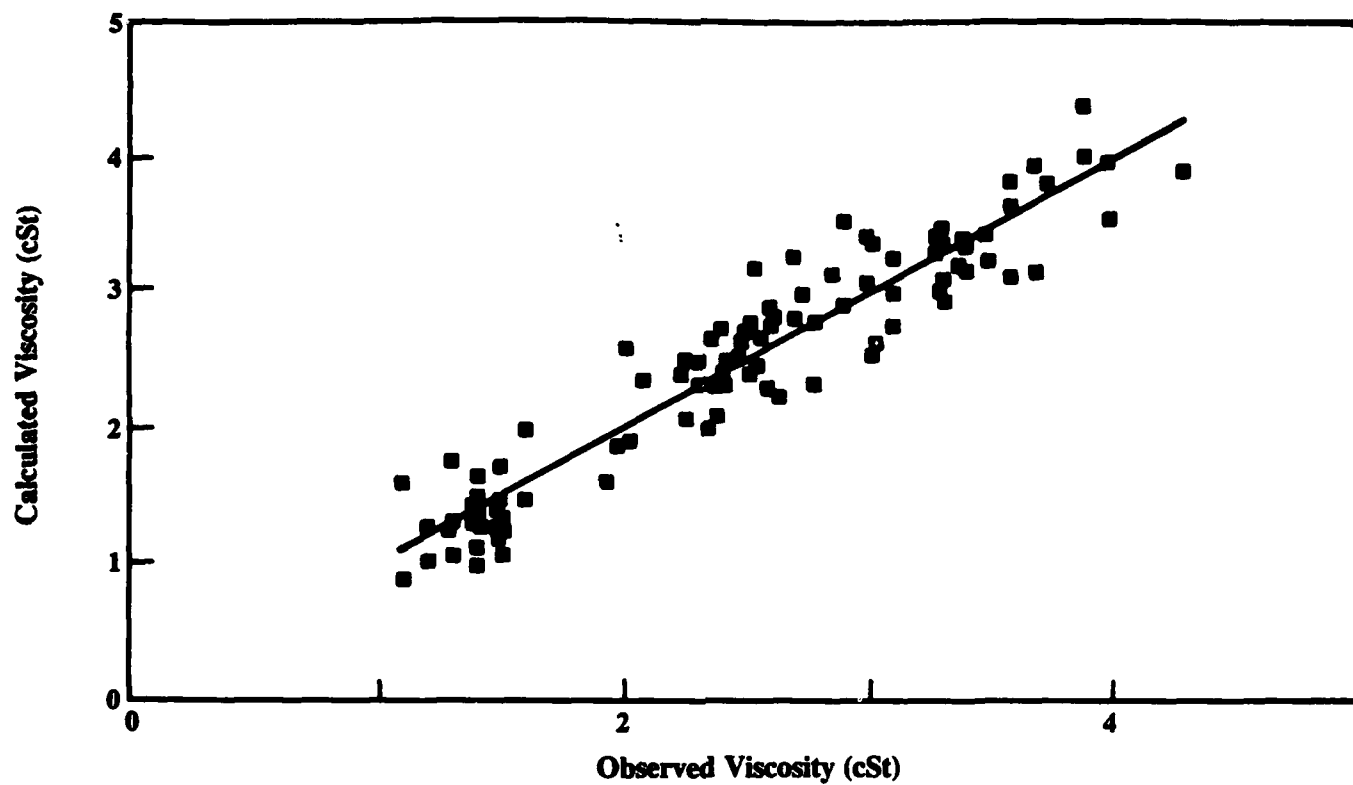
Figure 17. Correlation Plot for Viscosity
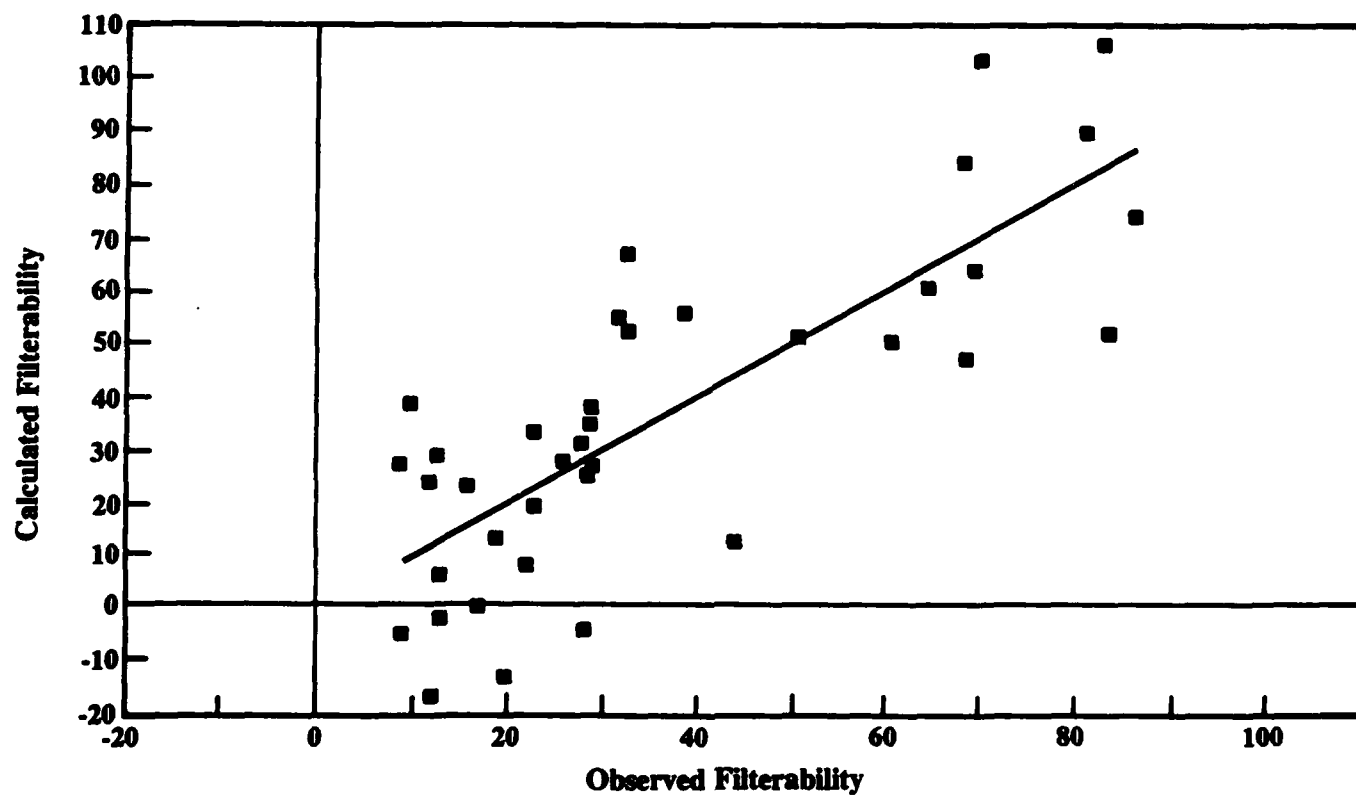
Figure 18. Correlation Plot for Filterability
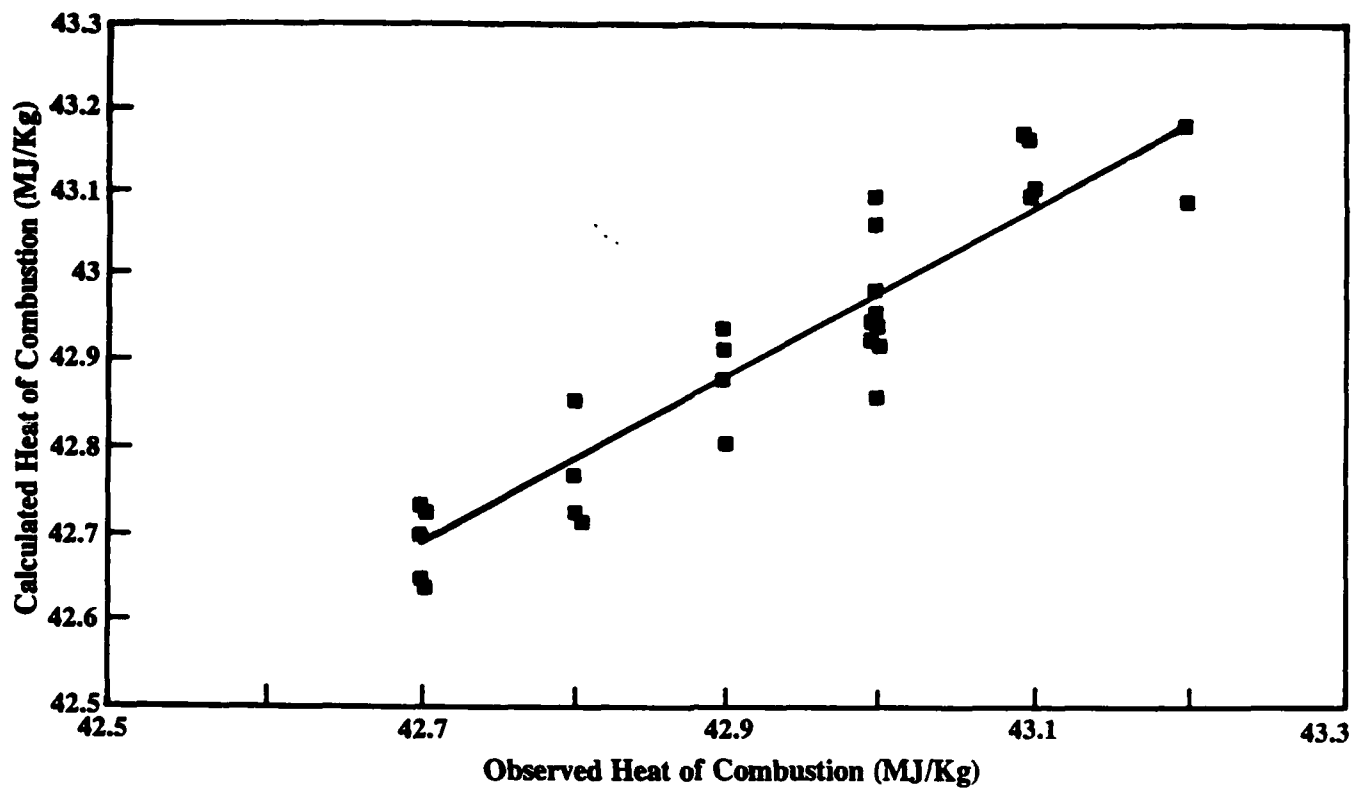
Figure 19. Correlation Plot for Heat of Combustion
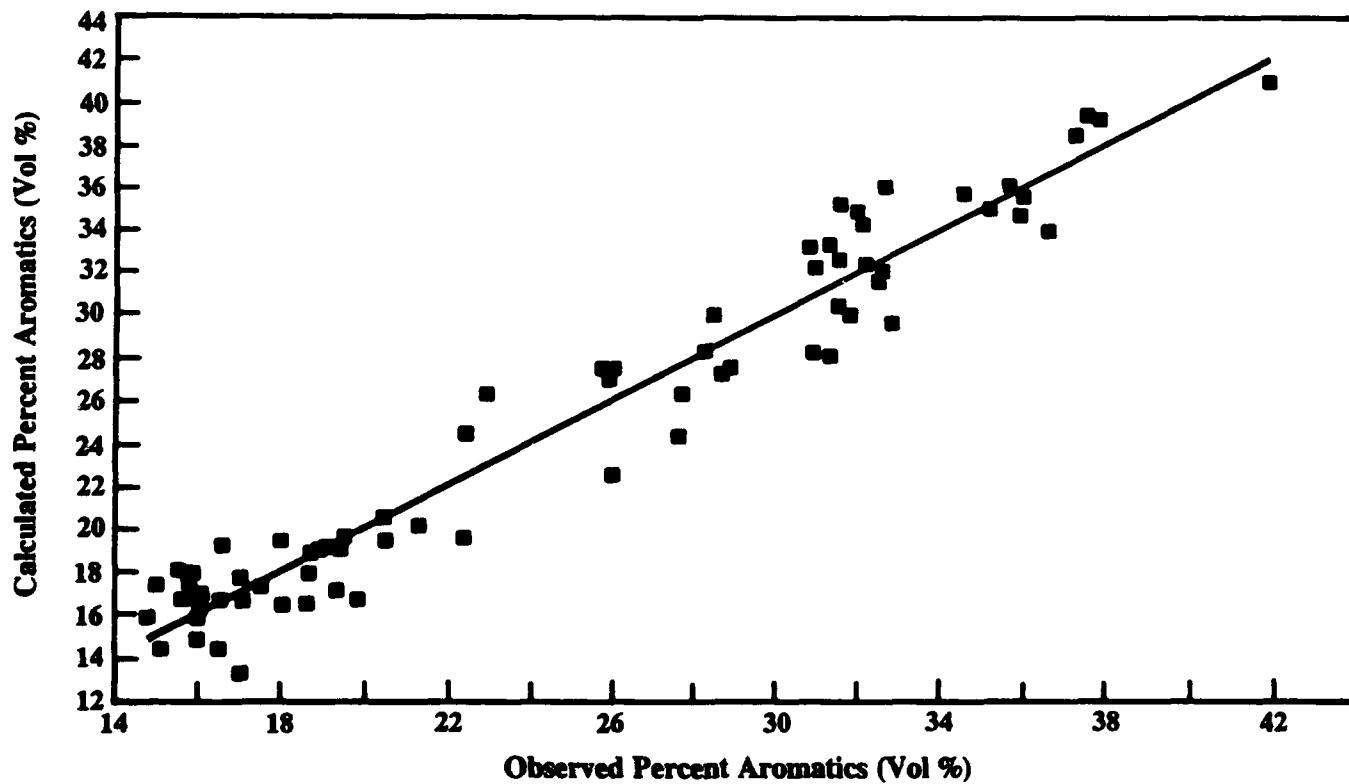
Figure 20. Correlation Plot for Percent Aromatics
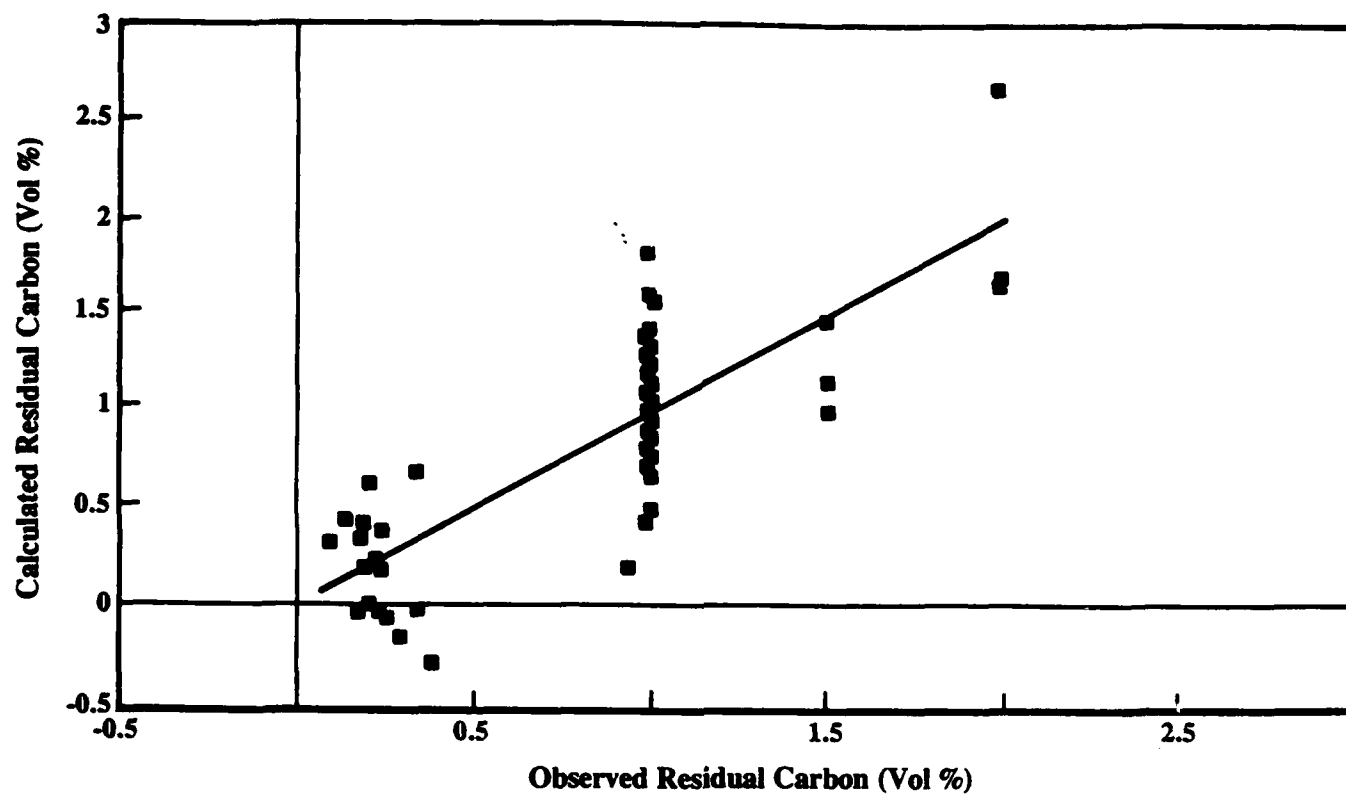
Figure 21. Correlation Plot for Residual Carbon
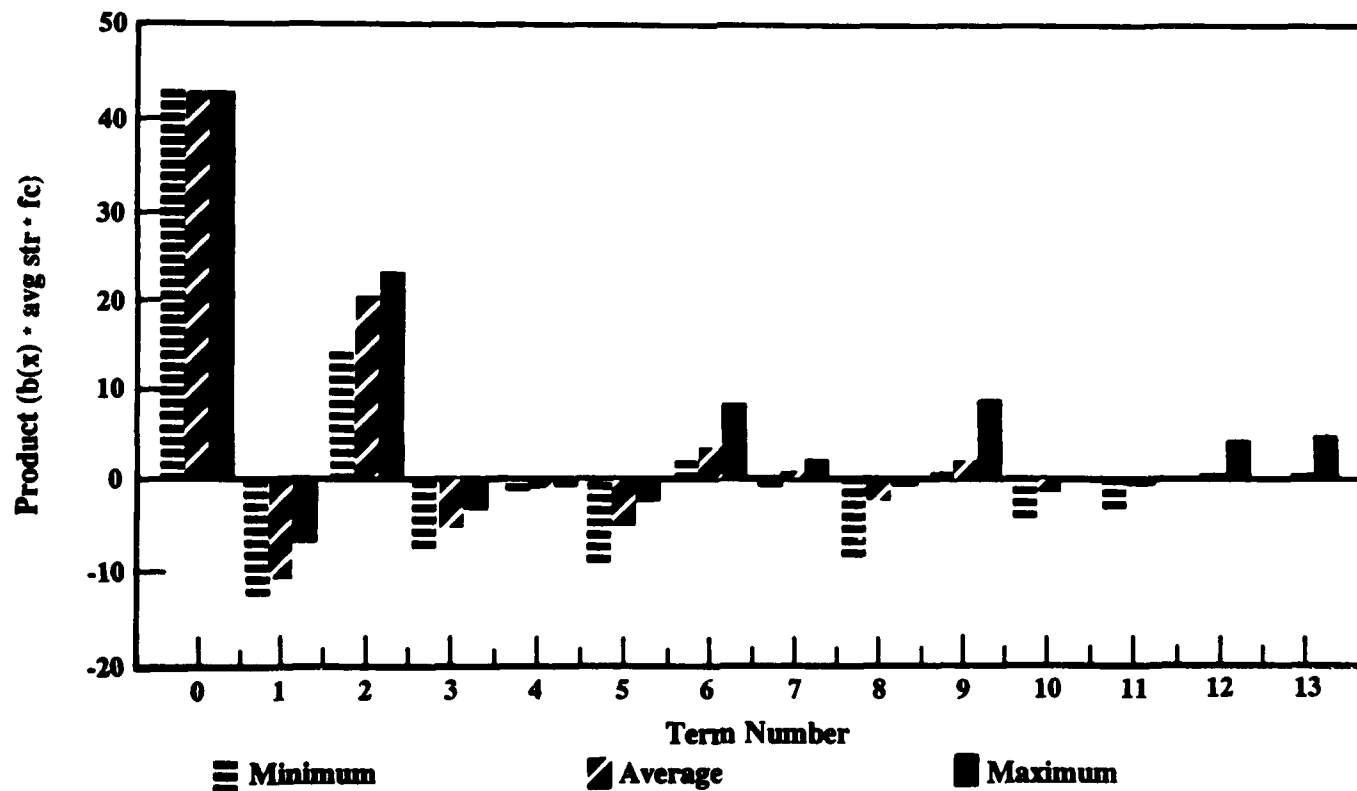
Figure 22. Distribution of Products Plot for Cetane Number
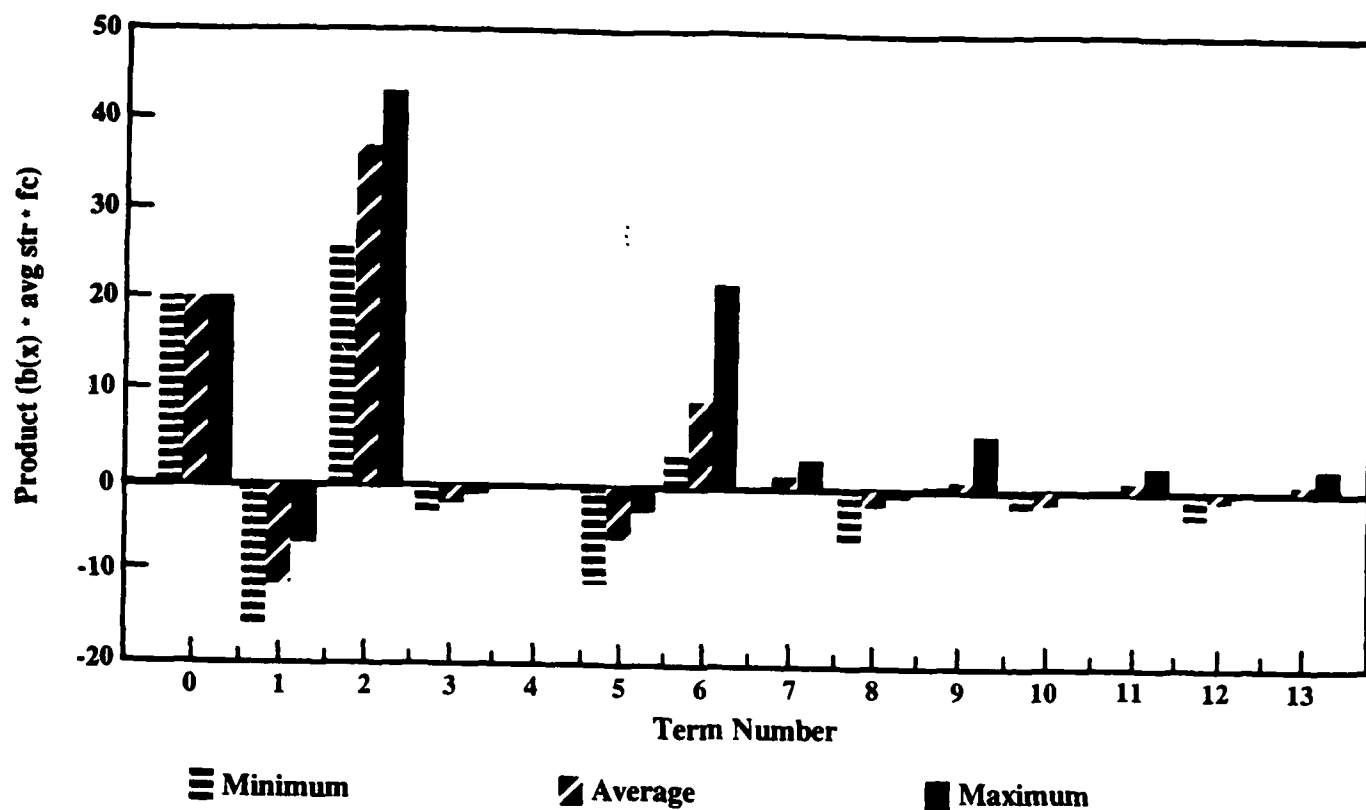
Figure 23. Distribution of Products Plot for Cetane Index
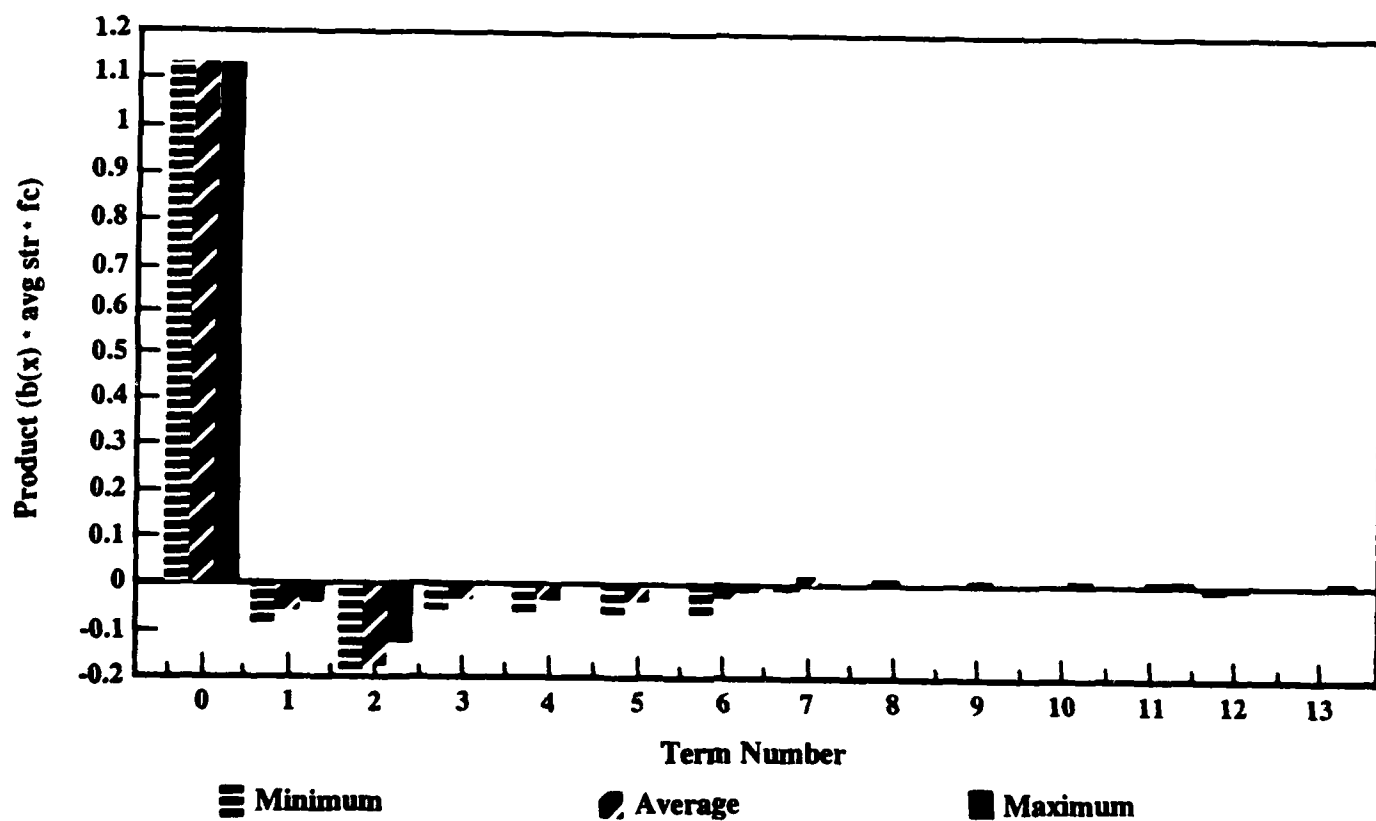
Figure 24. Distribution of Products Plot for Density
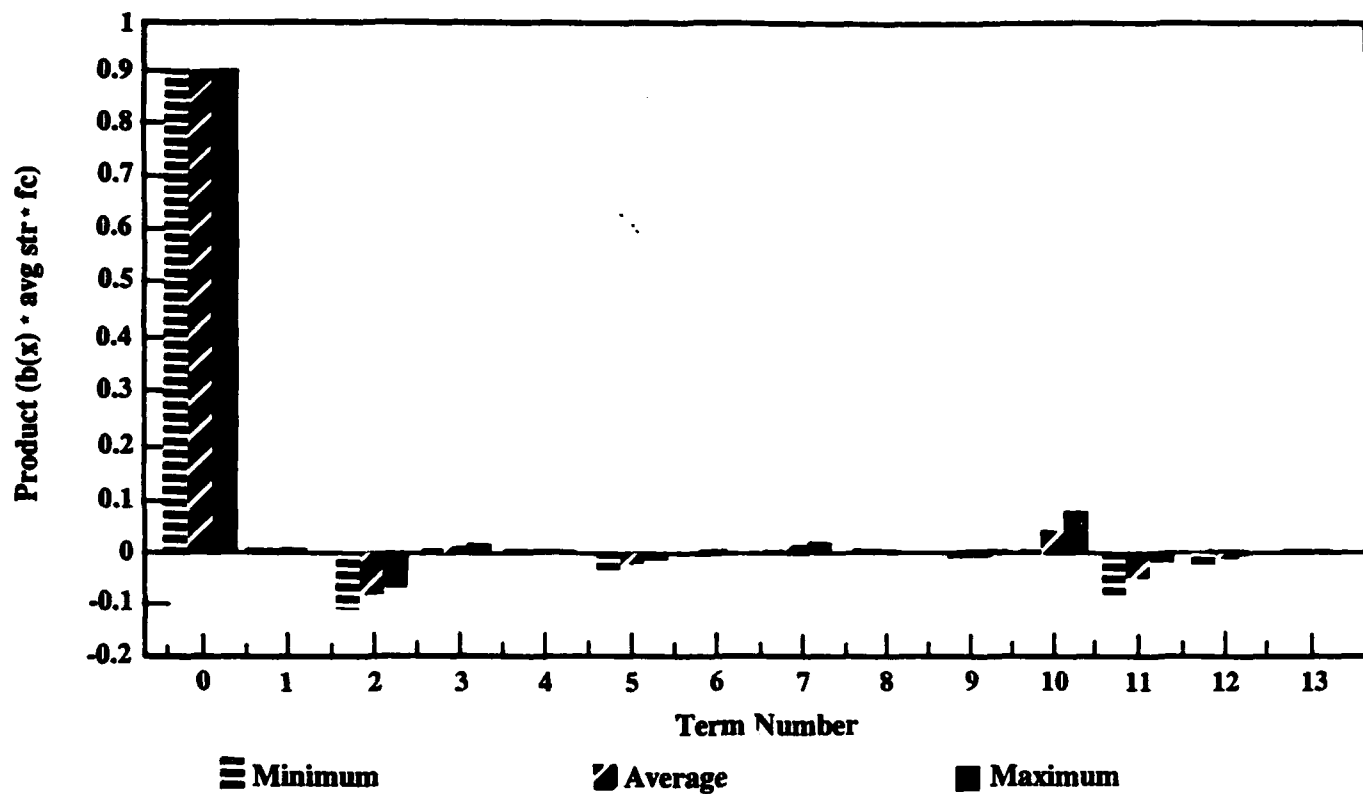
Figure 25. Distribution of Products Plot for Specific Gravity
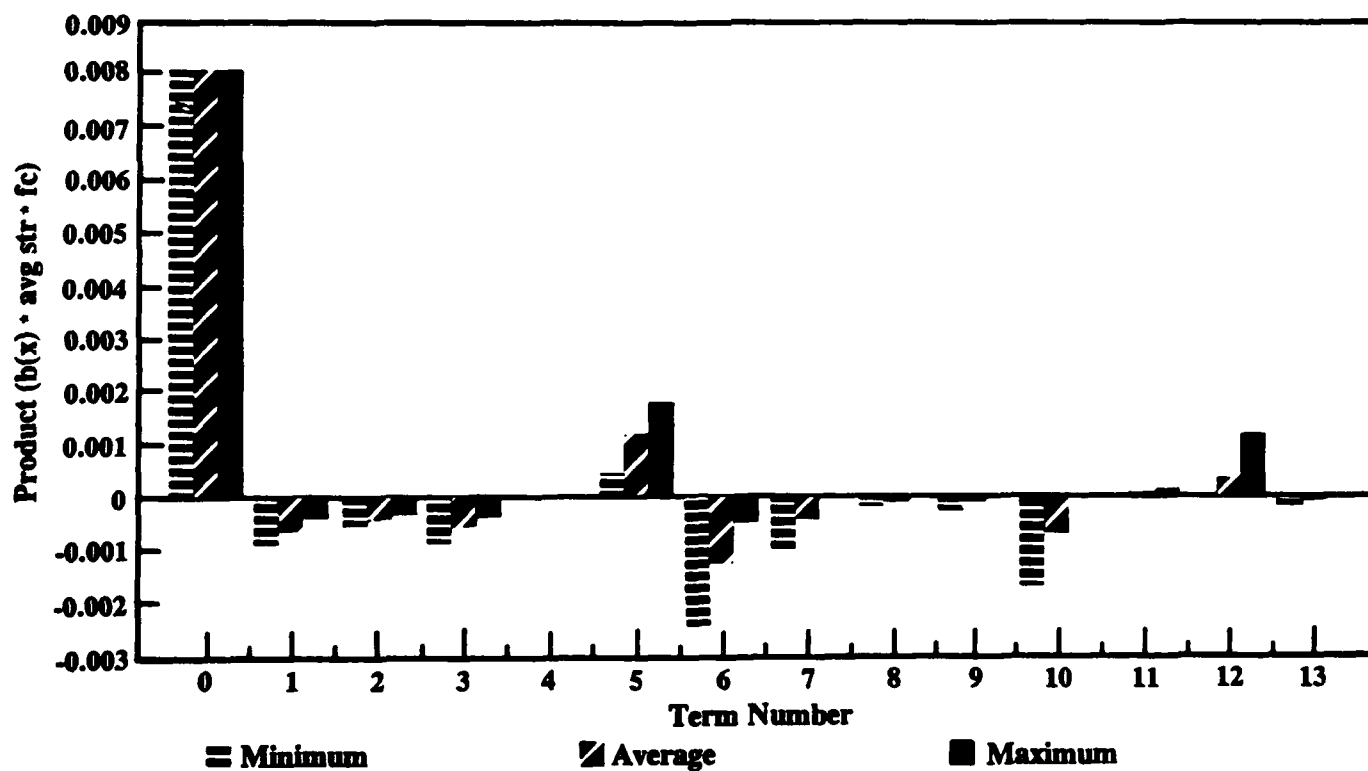
Figure 26. Distribution of Products Plot for Initial Boiling Point
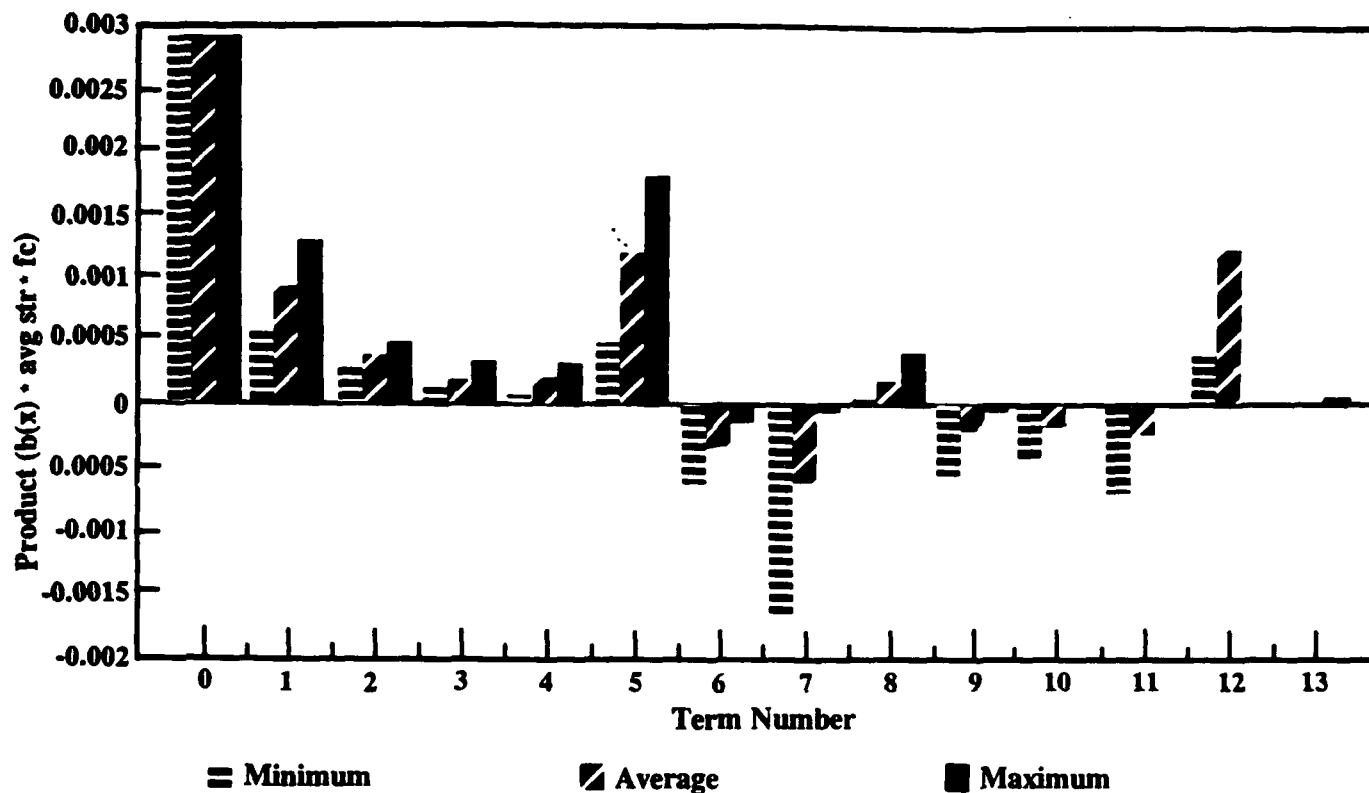
Figure 27. Distribution of Products Plot for Boiling Point: 10%
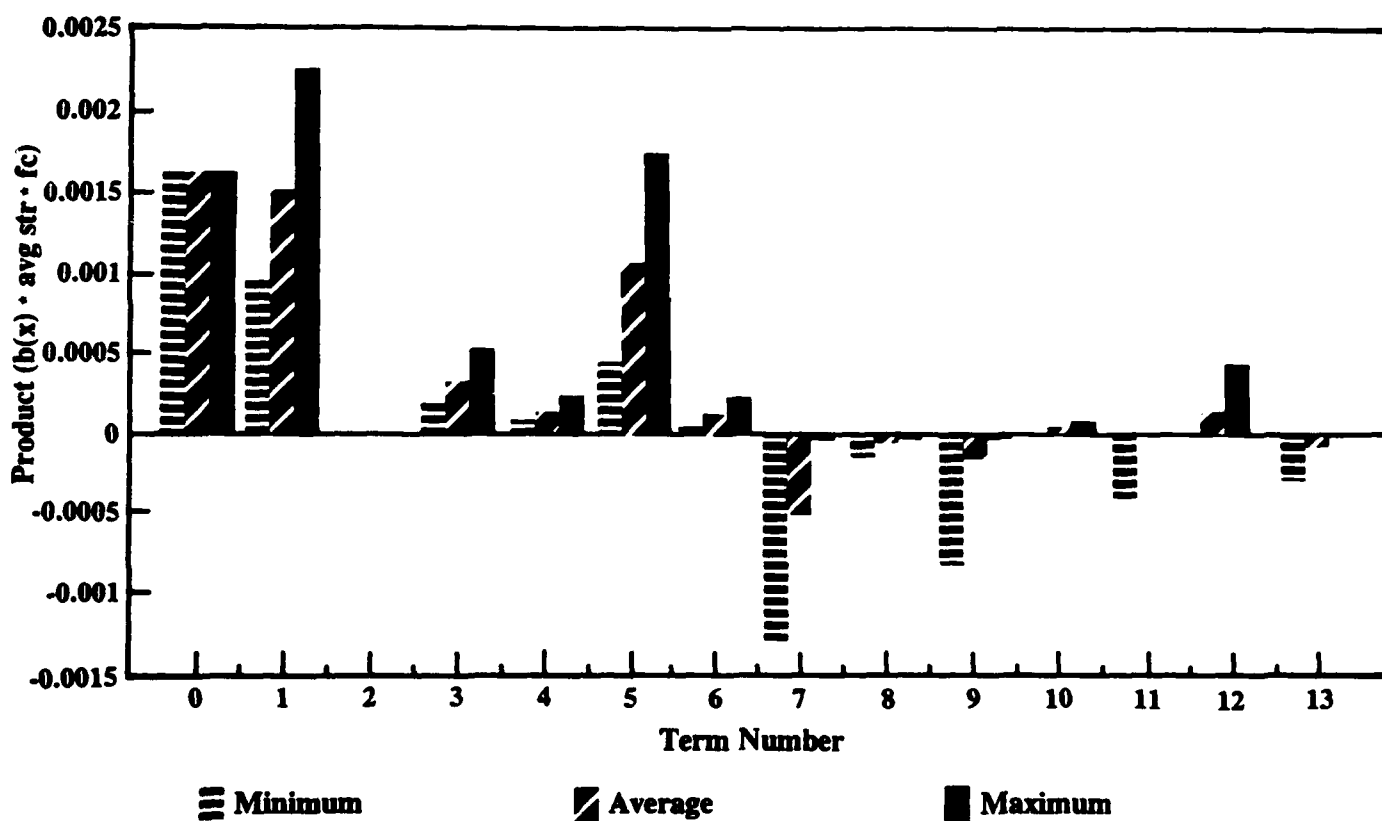
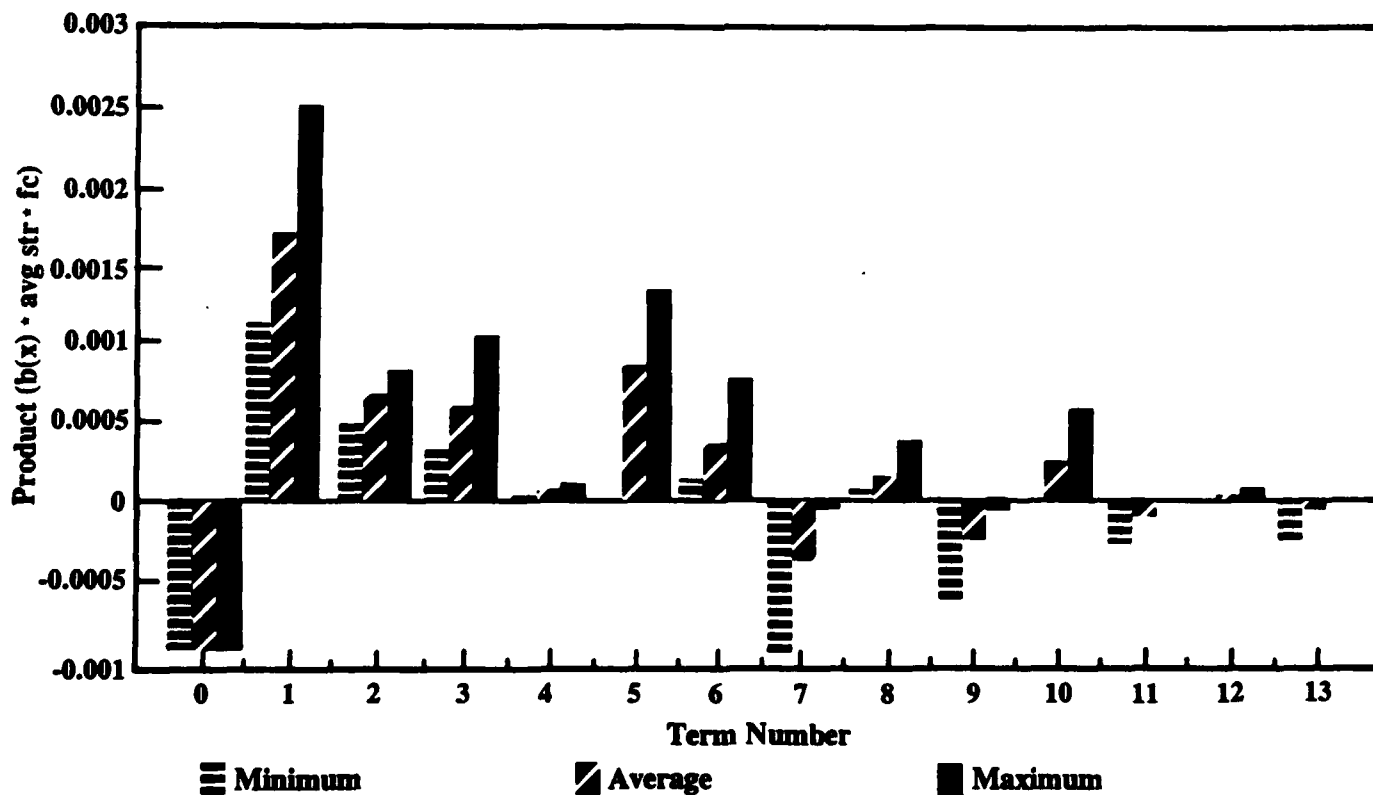**Figure 28. Distribution of Products Plot for Boiling Point: 50%**

A-16
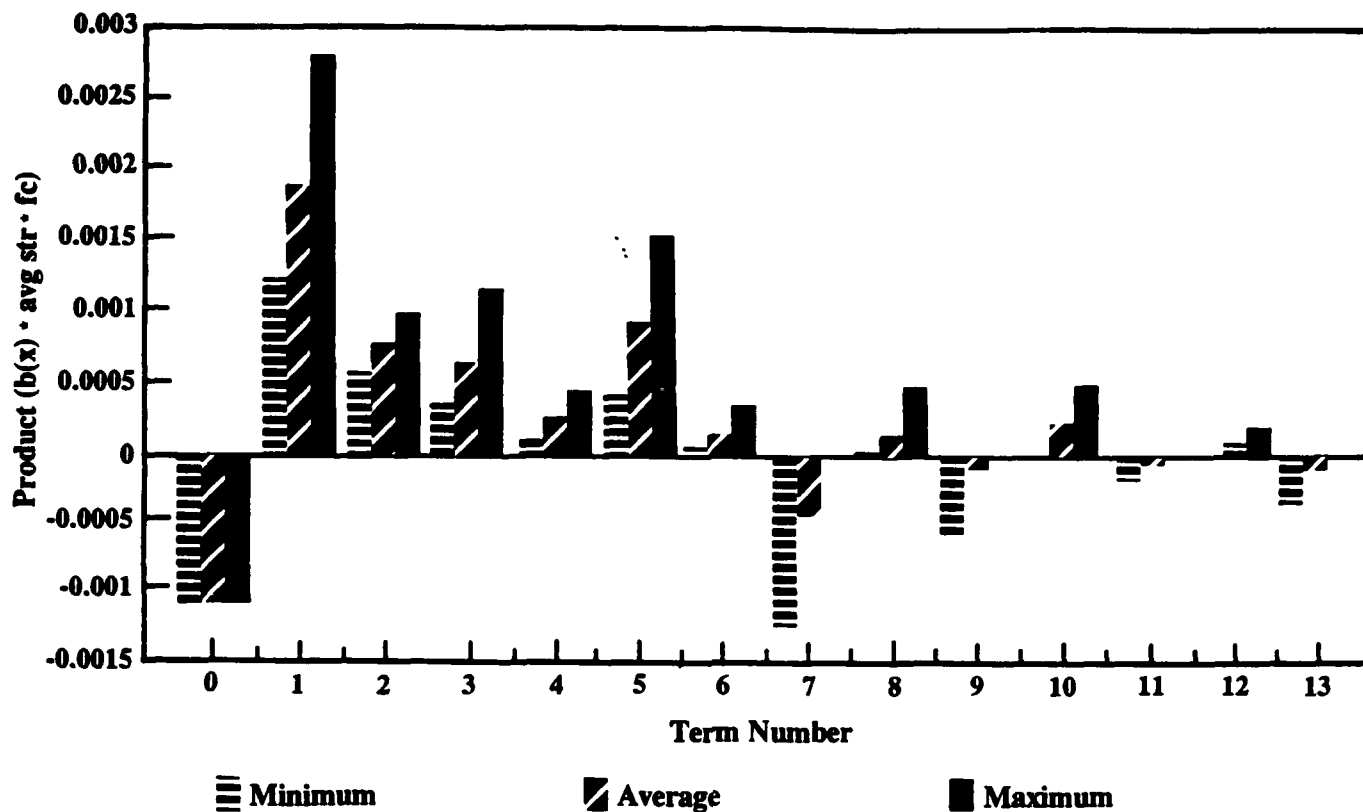
Figure 29. Distribution of Products Plot for Boiling Point: 90%

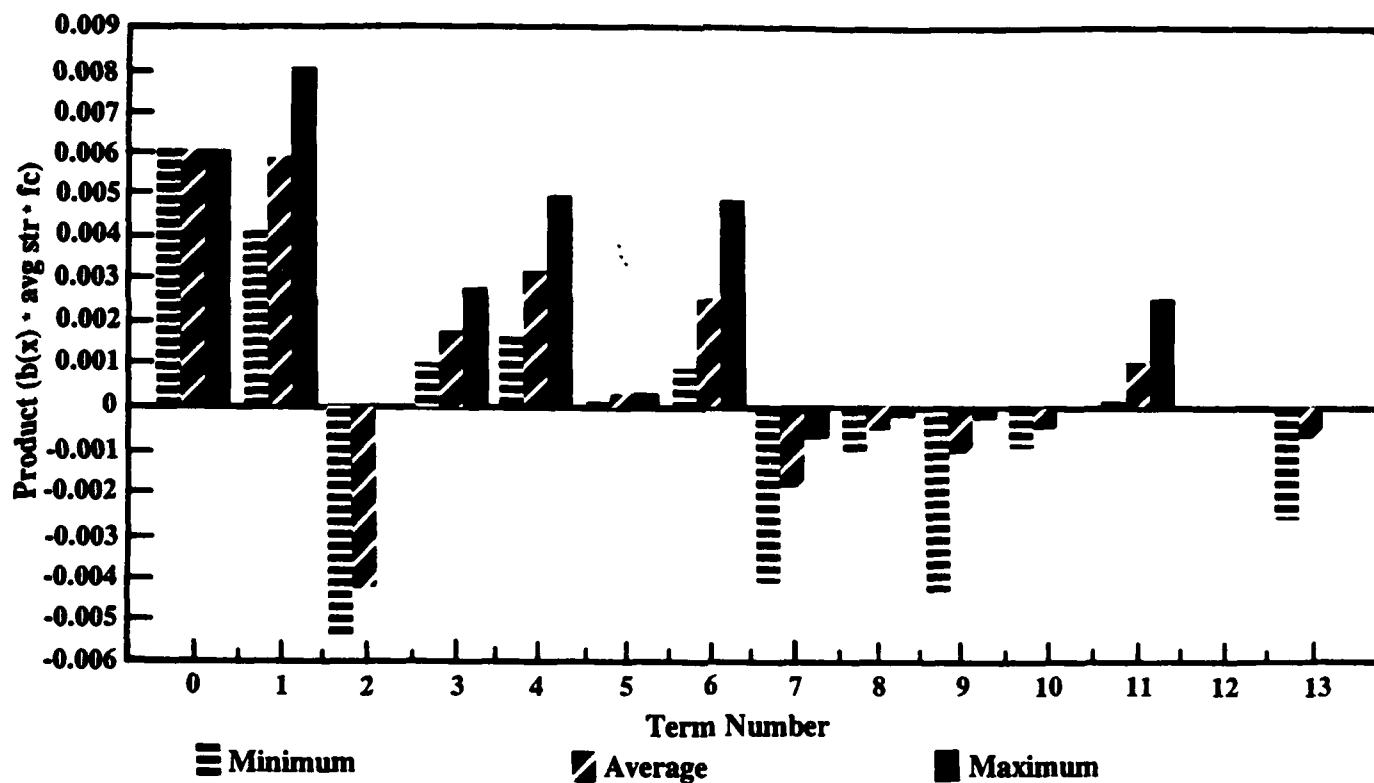**Figure 30. Distribution of Products Plot for End Boiling Point**

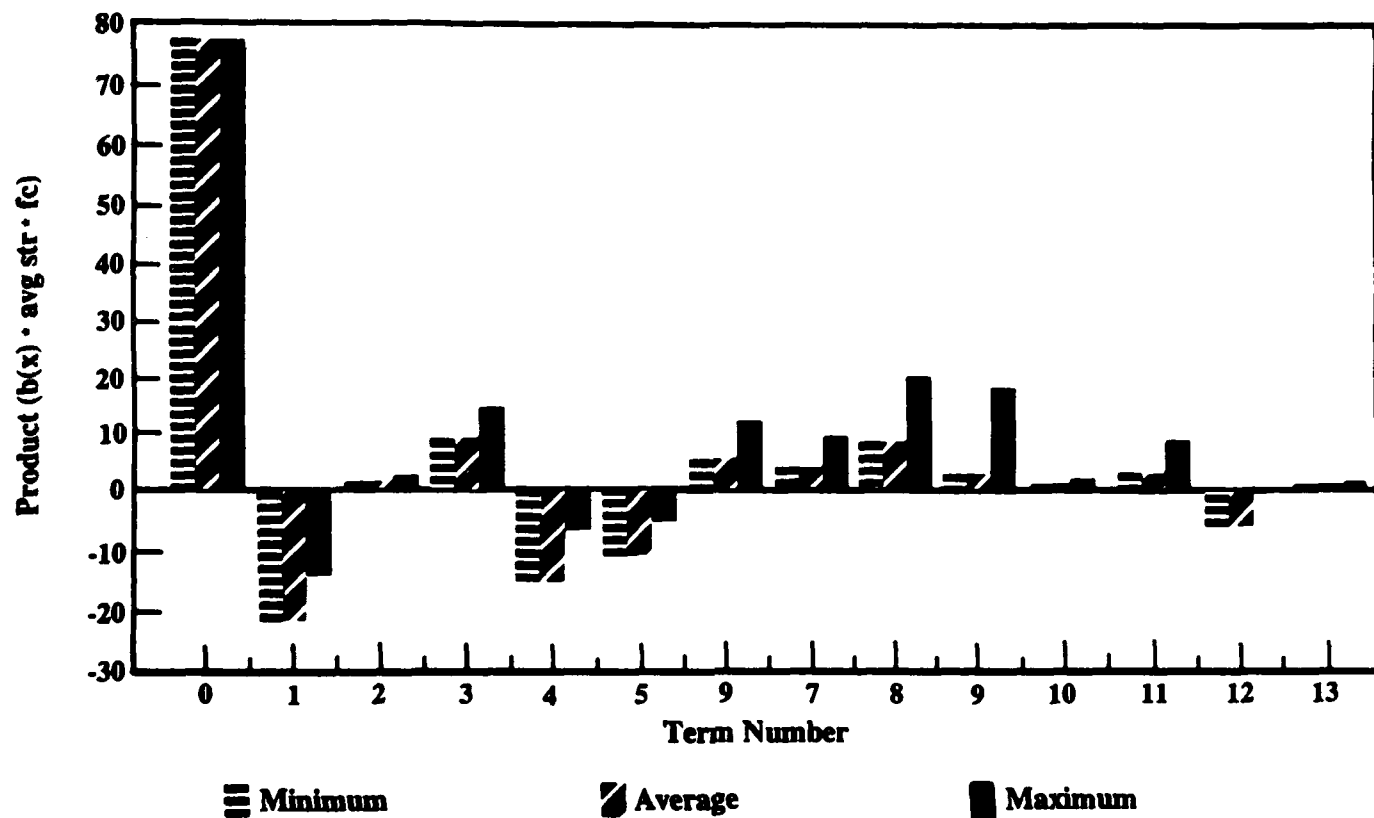**Figure 31. Distribution of Products Plot for Pour Point**

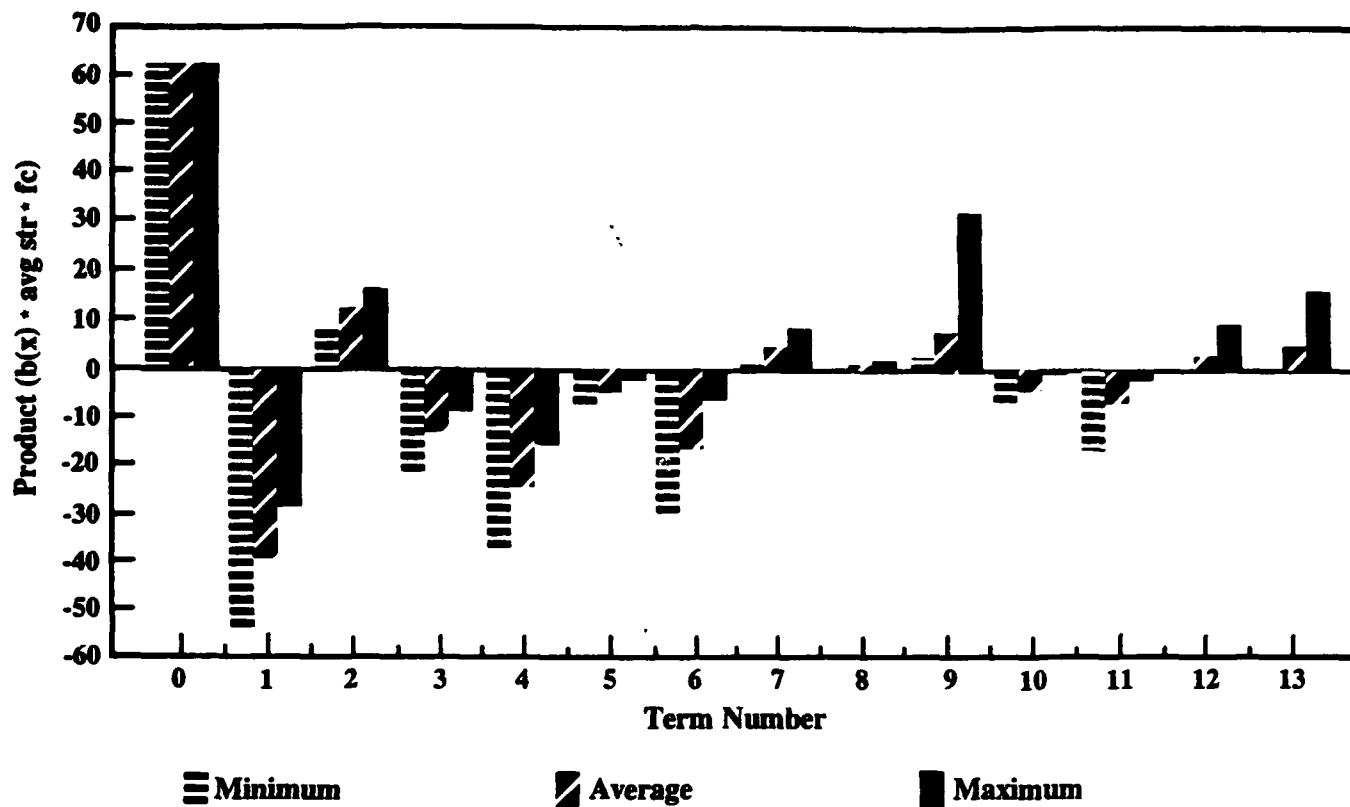**Figure 32. Distribution of Products Plot for Flash Point**
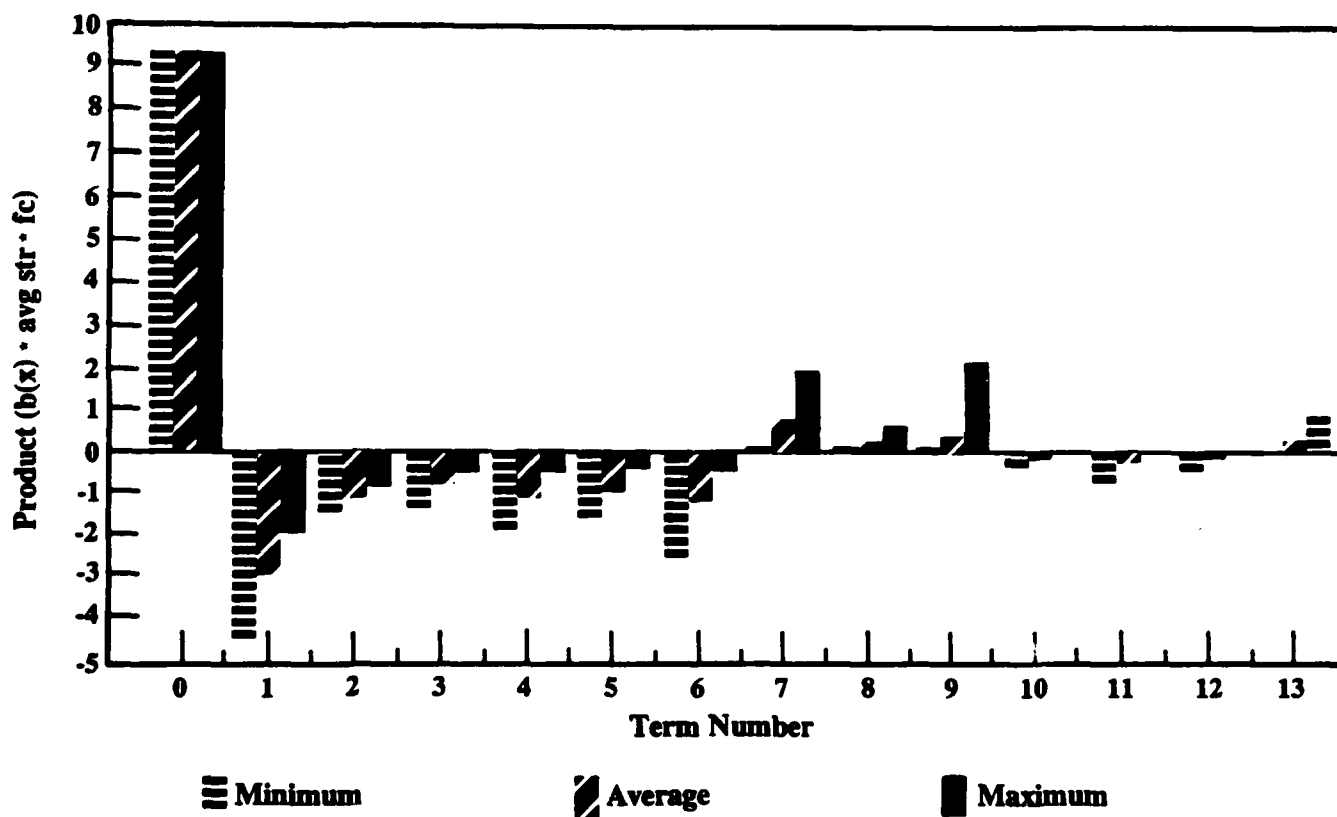
Figure 33. Distribution of Products Plot for Cloud Point
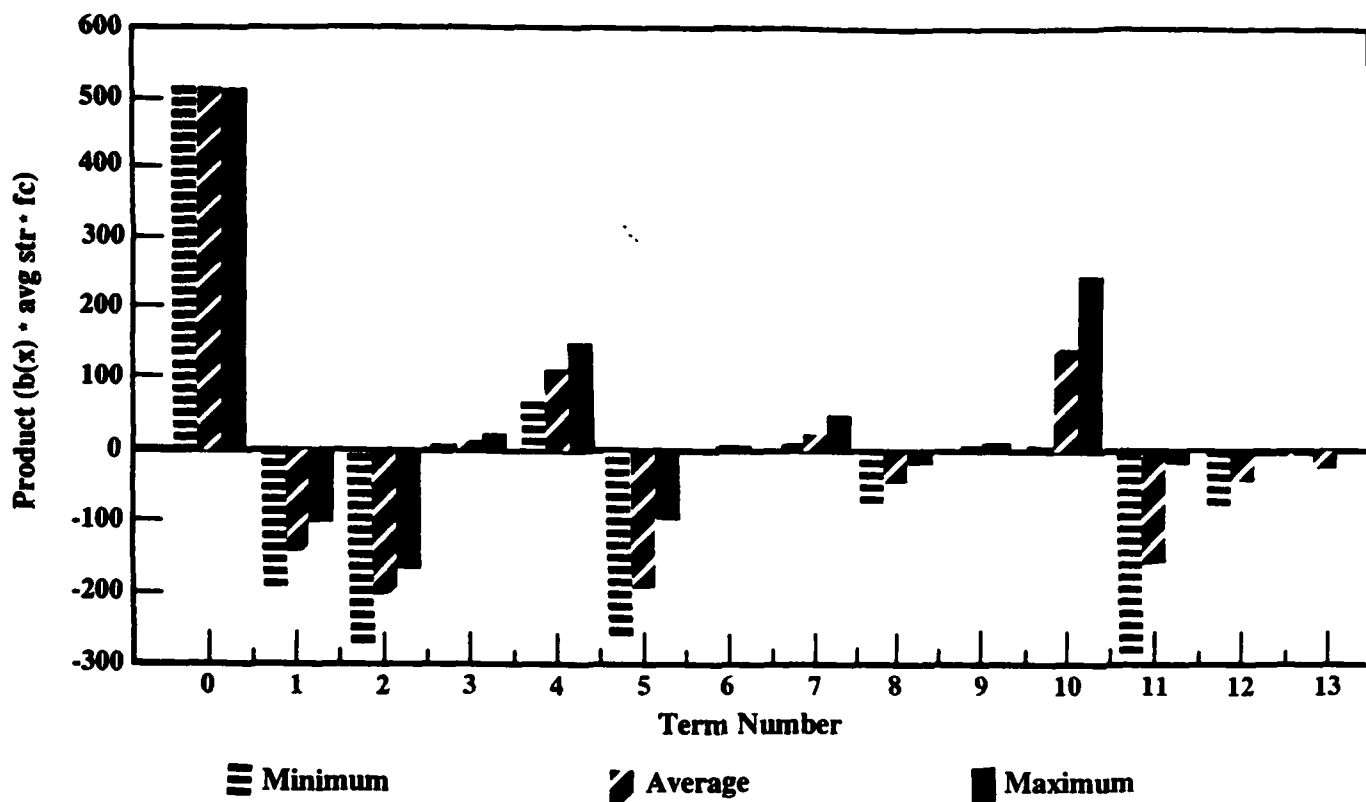

Figure 34. Distribution of Products Plot for Viscosity

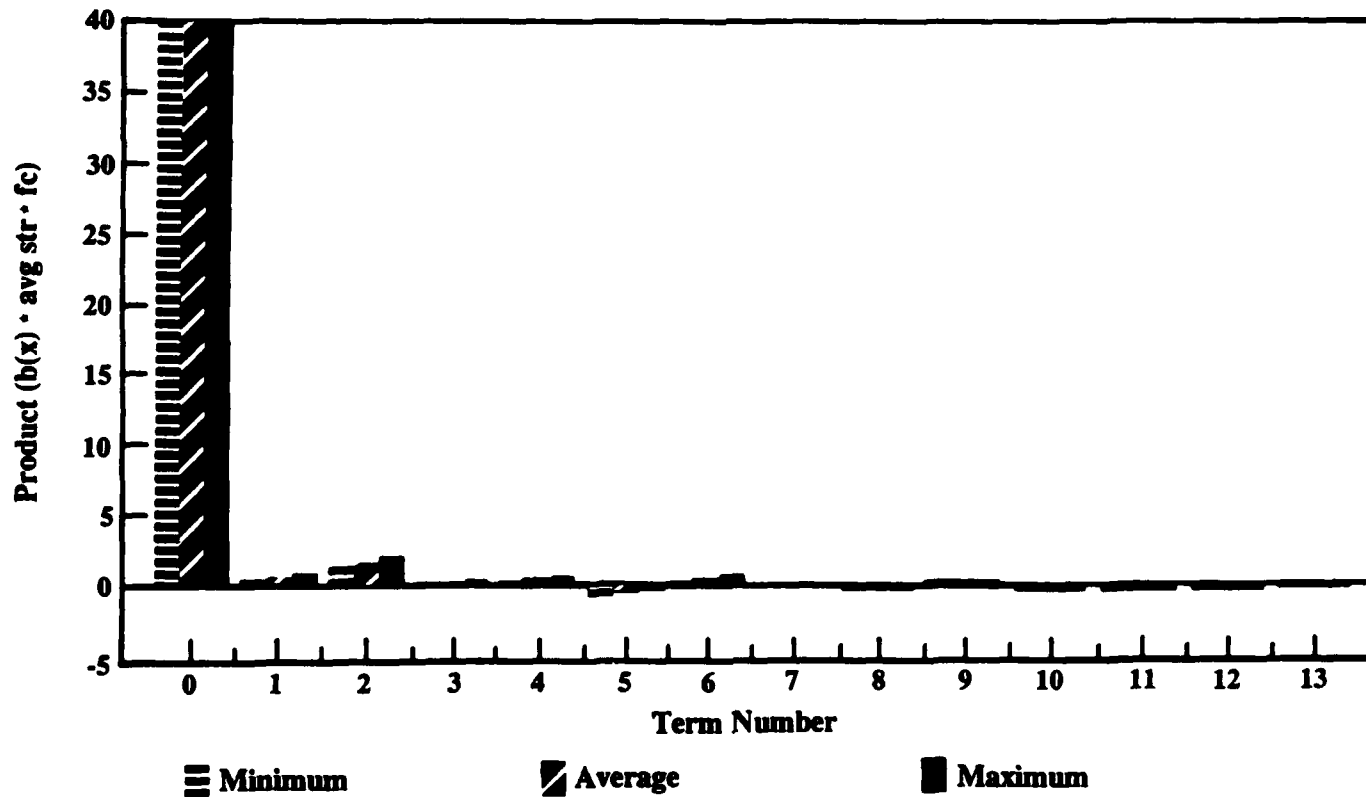**Figure 35. Distribution of Products Plot for Filterability**

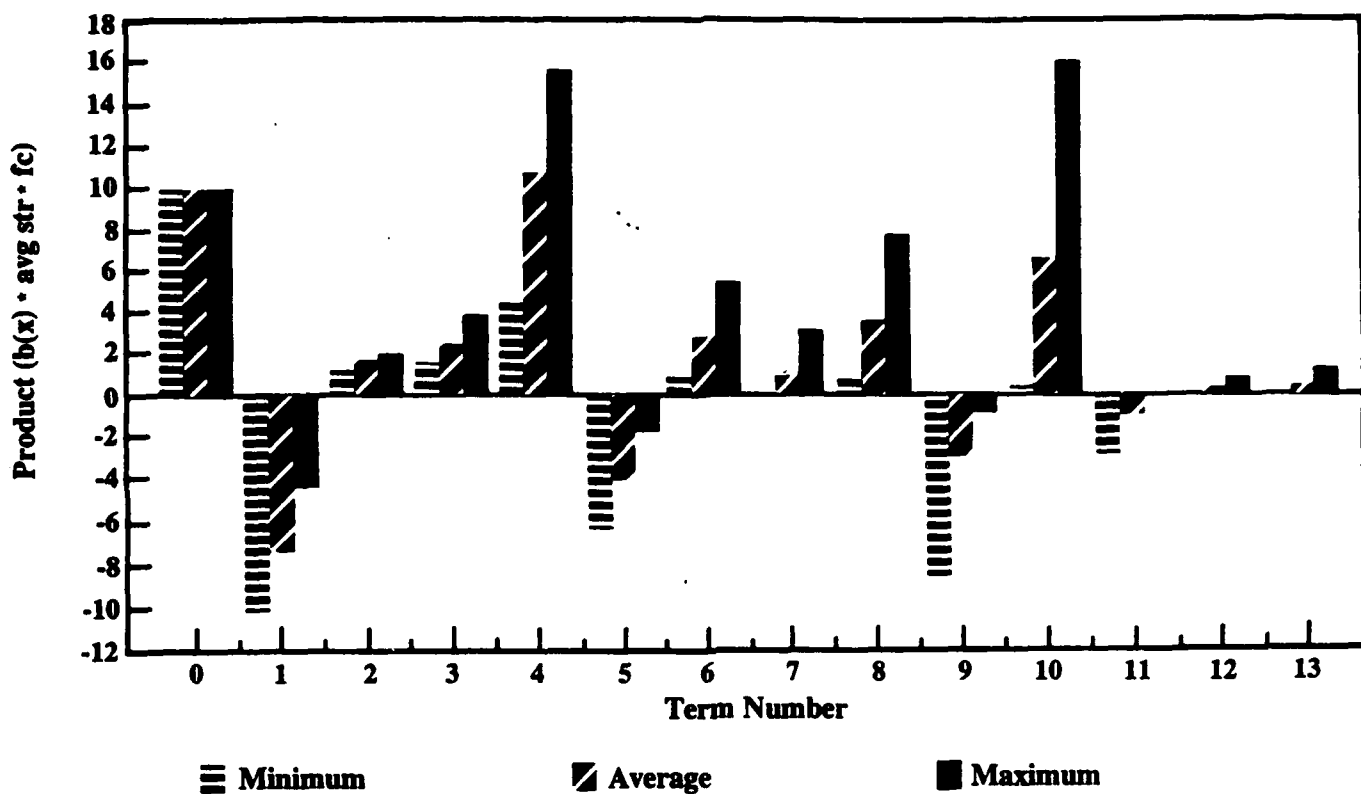**Figure 36. Distribution of Products Plot for Heat of Combustion**

A-20

Figure 37. Distribution of Products Plot for Percent Aromatics
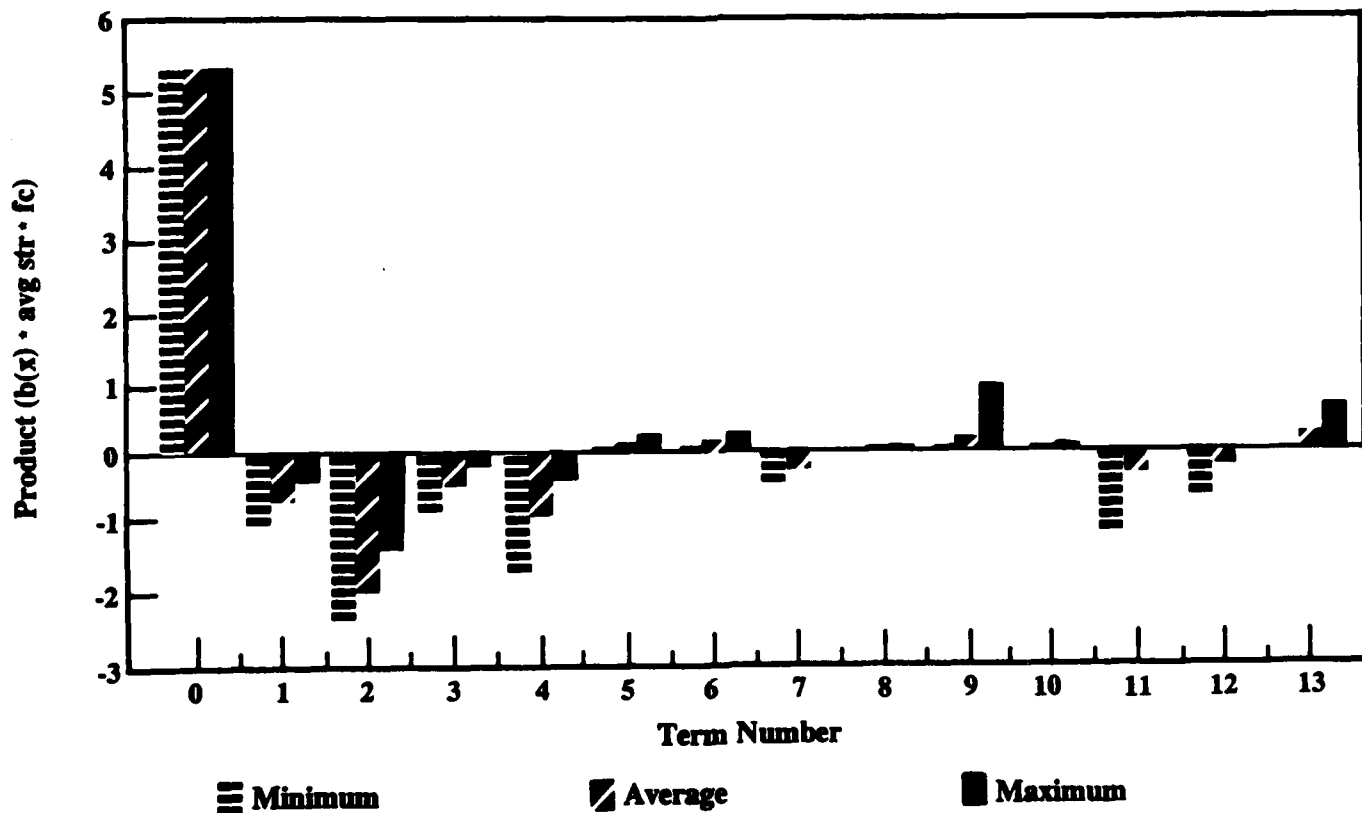

Figure 38. Distribution of Products Plot for Residual Carbon
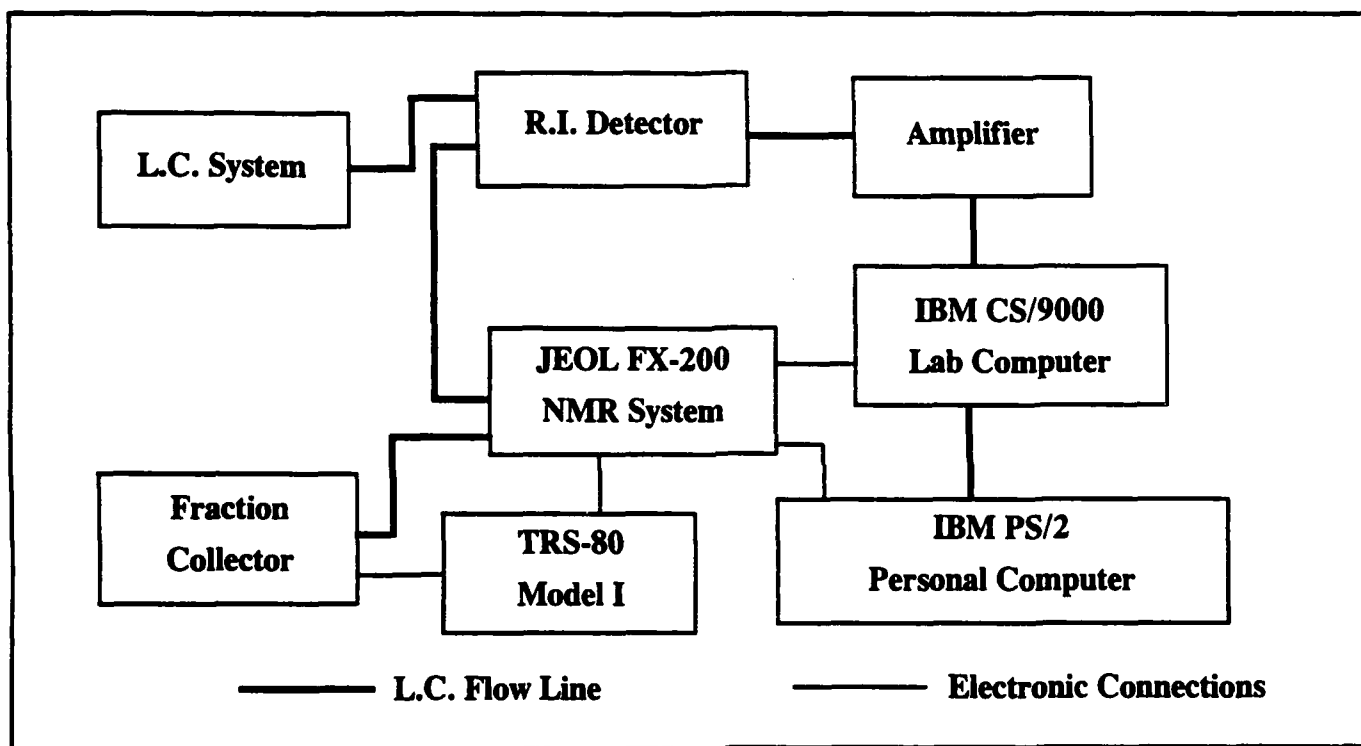
Figure 39. Block Diagram of Hardware of LC-^{1}H NMR System

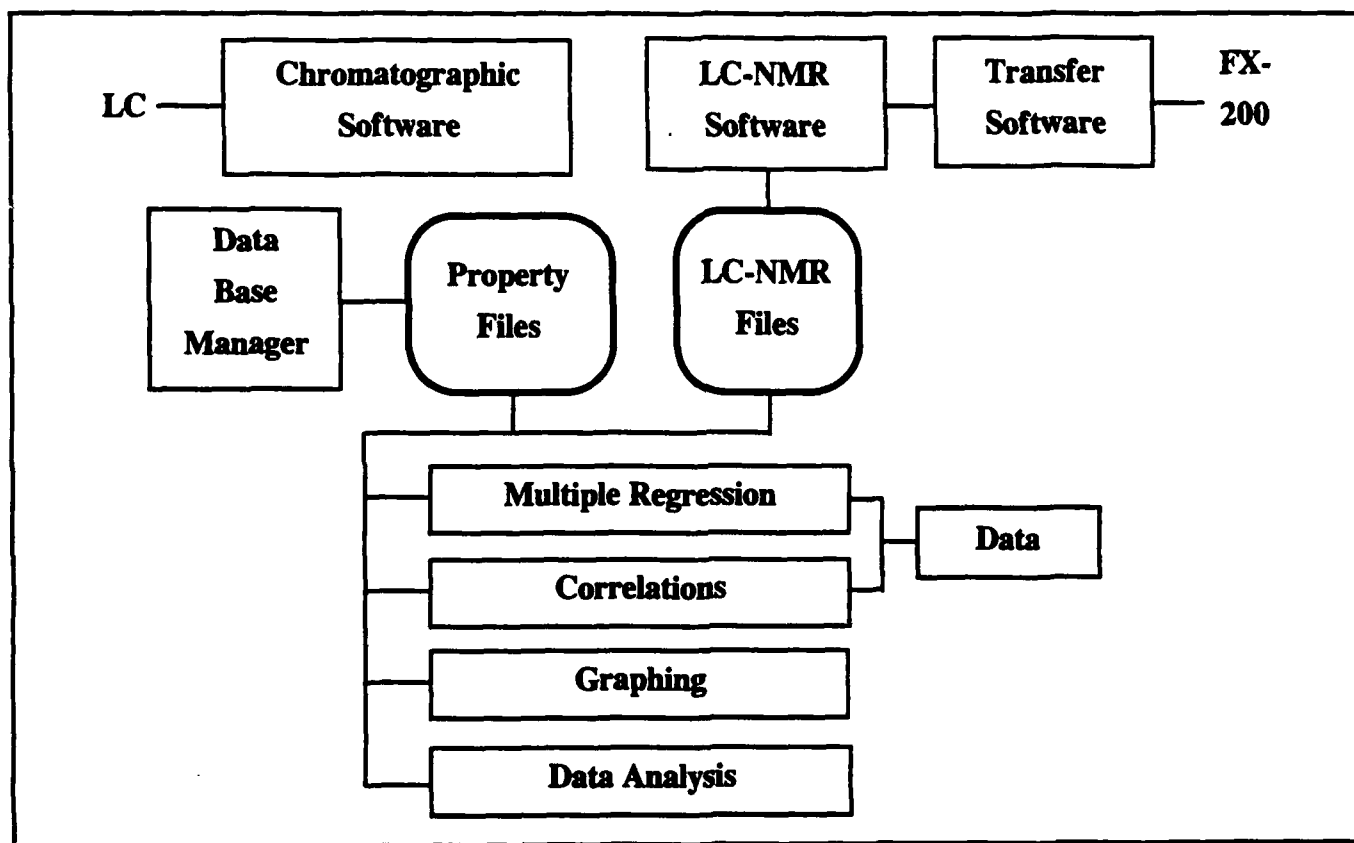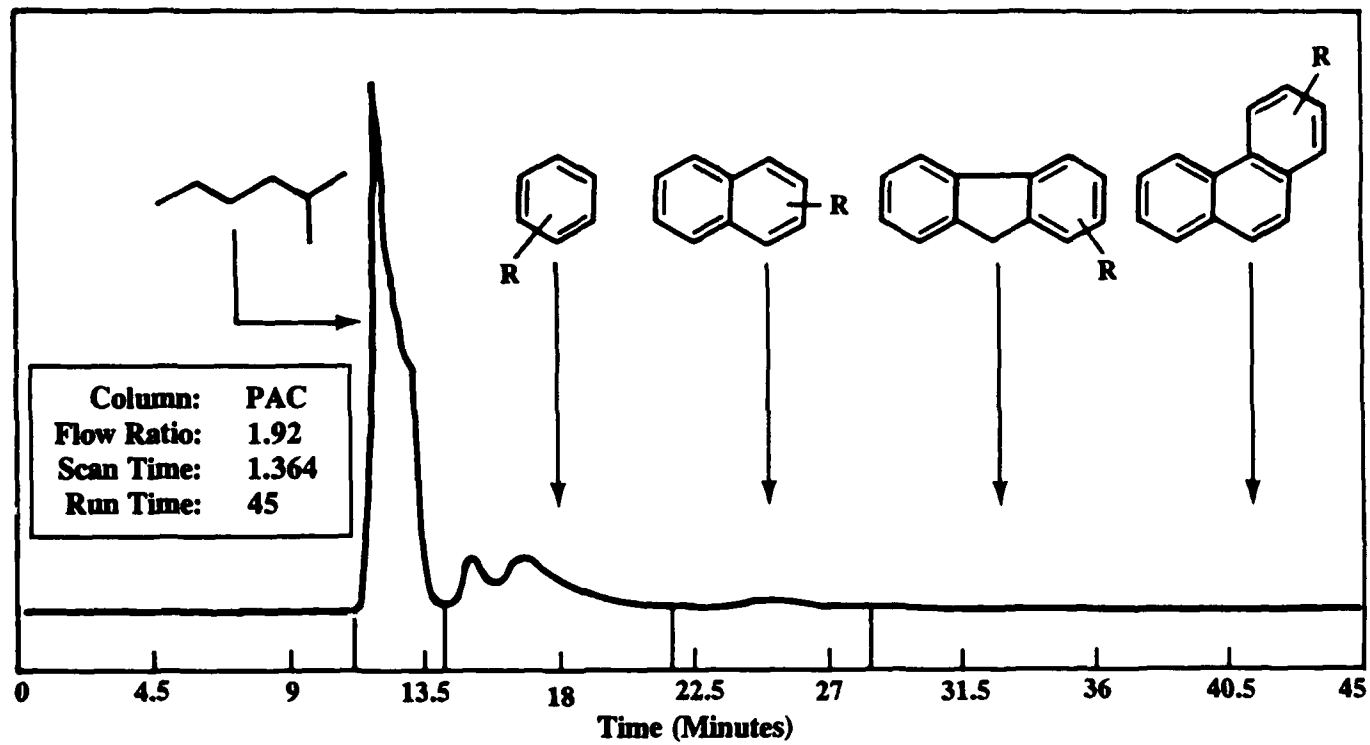Figure 40. Block Diagram of Software of LC-^{1}H NMR System

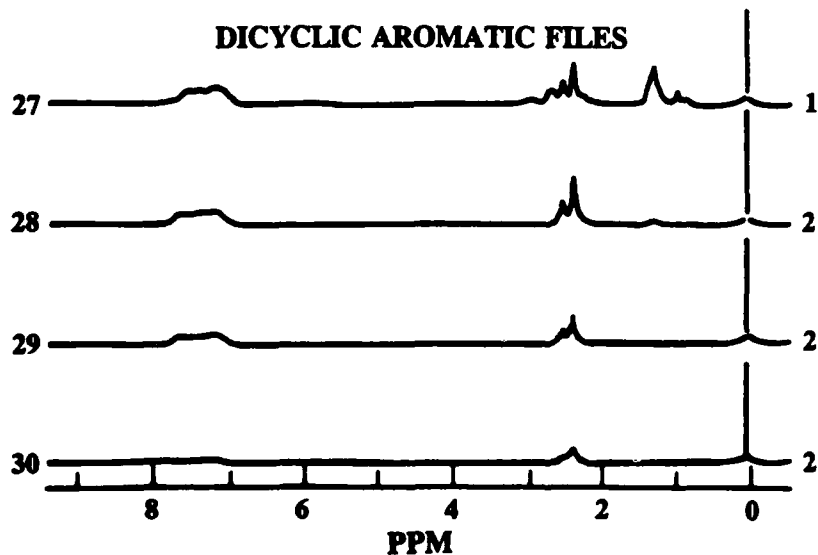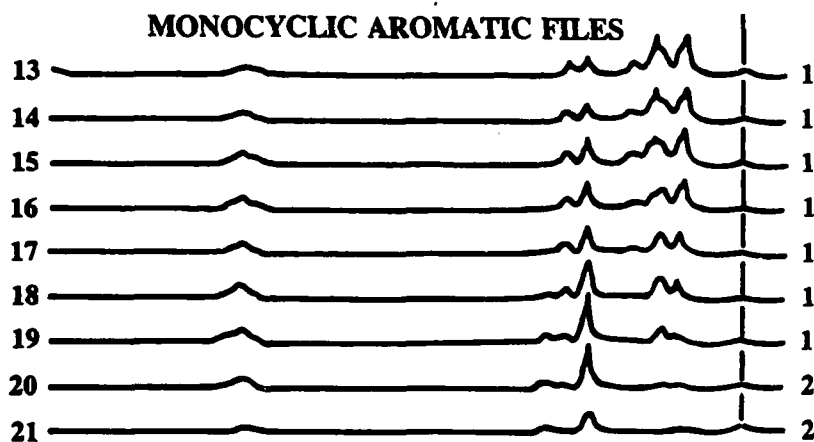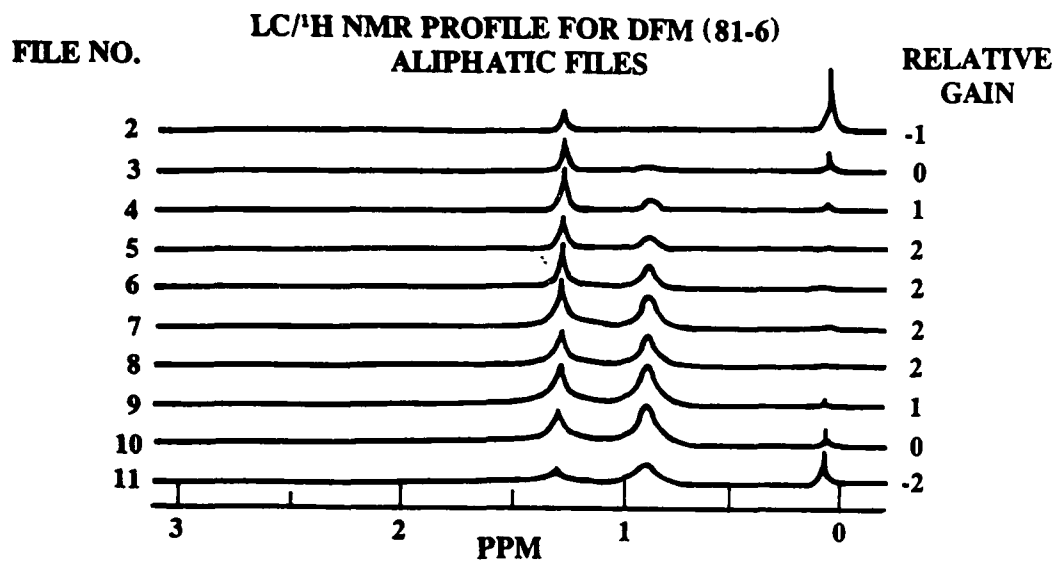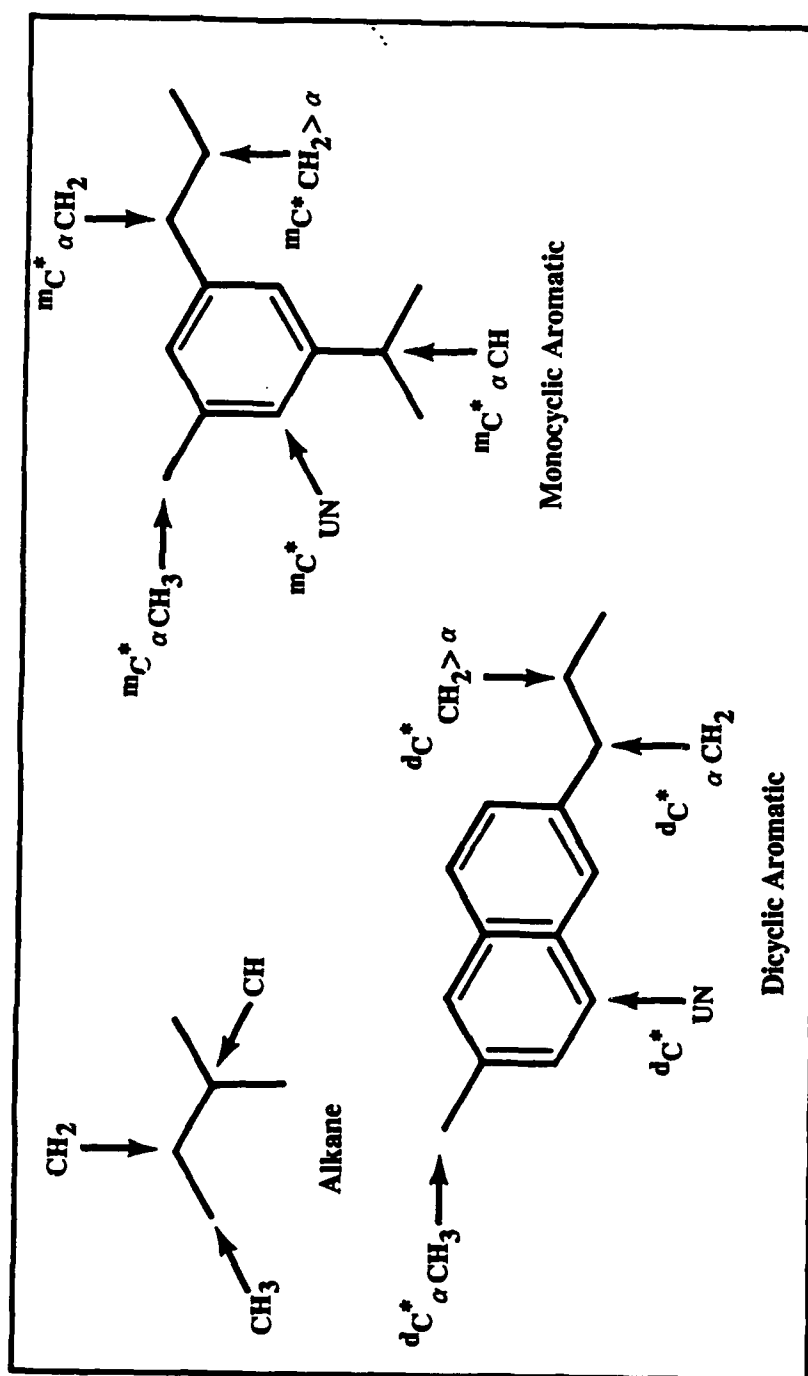Figure 41. Sample LC Spectrum

Figure 42. Sample ^{1}H NMR Spectrum

Figure 43. Chemical Structure Groups Present in Alkane, Monocyclic, and Dicyclic Chromatographic Fractions of Fuel

EXAMPLE OF DATA COLLECTED FOR EACH FUEL SAMPLE

Fuel: F14

Source: Army

Static NMR Data	^{13}C Aromaticity		^1H Aromaticity	
	FX-200	0.197	FX-200	0.067

LC–^{1} NMR Quantitative Data:

Average Structural Parameters for Monocyclic Aromatic Fraction:

$^*C_{un}^m$	$^*C_{sub}^m$	$^*C_{aCH_3}^m$	$^*C_{aCH_2}^m$	$^*C_{aCH}^m$	$^*C_{a\,tet}^m$	$^*C_{CH_2>a}^m$	$^*C_{CH_3>a}^m$	^mMW	^mADS
3.96	2.94	1.38	0.85	0.26	0.45	6.87	1.37	239.89	2.94

Average Structural Parameters for Dicyclic Aromatic Fraction:

$^*C_{un}^d$	$^*C_{sub}^d$	$^*C_{aCH_3}^d$	$^*C_{aCH_2}^d$	$^*C_{aCH}^d$	$^*C_{BH}^d$	$^*C_{CH_2>a}^d$	$^*C_{CH_3>a}^d$	^dMW	^dADS
6.33	1.77	1.50	0.27	0.00	2.00	0.09	-0.27	167.62	1.77

Average Structural Parameters for Fluorene Fraction:

$^*C_{un}^f$	$^*C_{sub}^f$	$^*C_{aCH_3}^f$	$^*C_{aCH_2}^f$	$^*C_{aCH}^f$	$^*C_{BH}^f$	$^*C_{CH_2>a}^f$	$^*C_{CH_3>a}^f$	^fMW	^fADS
5.12	2.88	2.42	1.46	0.00	4.00	0.04	0.46	225.38	2.88

Average Structural Parameters for Phenanthrene Fraction:

$^*C_{un}^p$	$^*C_{sub}^p$	$^*C_{aCH_3}^p$	$^*C_{aCH_2}^p$	$^*C_{aCH}^p$	$^*C_{BH}^p$	$^*C_{CH_2>a}^p$	$^*C_{CH_3>a}^p$	^pMW	^pADS
7.93	2.07	1.57	0.50	0.00	4.00	0.65	0.50	233.54	2.07

Fuel: F14
Source: Army

Absolute Number of Moles of Carbon and Fractional Aromaticity Data

	$C_{Ar\ total}$	C_{total}	f_a	F_{total}
Alkanes		0.0037213		0.604
Monocyclic Aromatics	0.0005866	0.0016355	0.132	0.265
Dicyclic Aromatics	0.00005690	0.0007205	0.058	0.117
Fluorenes	0.0000259	0.0000401	0.003	0.007
Phenanthrenes	0.0000358	0.0000474	0.004	0.008

$$f_a = 0.197$$

Comments:

Other Physical Data

Predicted Smoke Point:
Predicted Freezing Point:

Aromaticity:
<Volume % >

Elemental Analysis:	C	H	H (by NMR)

DISTRIBUTION FOR REPORT NO. 2478

DEPARTMENT OF DEFENSE

1   Director, Technical Information
Defense Advanced Research Projects
   Agency
1400 Wilson Blvd.
Arlington, VA 22209

1   Director
Defense Nuclear Agency
ATTN: TITL
Washington, DC 20305

2   Defense Technical Information Center
Cameron Station
ATTN: DTIC-FDAC
Alexandria, VA 22304-6145

DEPARTMENT OF THE ARMY

1   HQDA (DAMA-AOA-M)
Washington, DC 20310

1   HQDA (DALO-TSM)
Washington, DC 20310

1   HQDA (DAEN-RDL)
Washington, DC 20314

1   HQDA (DAEN-MPE-T)
Washington, DC 20314

1   Commander
US Army Missile Research & Development
   Command
ATTN: AMSMI-PR
Redstone Arsenal, AL 35809

1   Director
Army Materials and Mechanics Research
   Center
ATTN: AMXMR-RL Technical Library
Watertown, MA 02172-0001

1   Commander
Chemical Research R&D Center
ATTN: SMCCR-SPS (Tech Library)
Aberdeen Proving Ground, MD 21005

1   Commander
US Army Aberdeen Proving Ground
ATTN: STEAP-MT-U (GE Branch)
Aberdeen Proving Ground, MD 21005

1   Director
US Army Materiel Systems Analysis Agency
ATTN: AMXSY-MP
Aberdeen Proving Ground, MD 21005-5071

1   Director
US Ballistics Research Laboratory
ATTN: AMXBR-OD-ST (STINFO)
Aberdeen Proving Ground, MD 21005-5066

1   Director
US Army Engineer Waterways Experiment
   Station
ATTN: Chief, Library Branch
         Technical Information Center
Vicksburg, MS 39180

1   Commander
US Army Armament Research &
   Development Command
ATTN: SMCAR-TSS
Dover, NJ 07801-5001

1   Commander
US Army Troop Support & Aviation
   Materiel Readiness Command
ATTN: DRSTS-MES (1)
4300 Goodfellow Blvd.
St. Louis, MO 63120

2   Director
Petrol & Fld Svc Dept
US Army Quartermaster School
Fort Lee, VA 23801

1	US Army Tank Automotive Command ATTN: DRSTA-TSL Warren, MI 48090	1	HQDA ODCSLOG DALO-TSE Room 1E588, Pentagon Washington, DC 20310-0561
1	US Army Laboratory Command ATTN: M. Levy SLCMT-MN Materials Technology Laboratory Watertown, MA 02172-0001	1	Plastics Technical Evaluation Center ARRADCOM, Bldg 3401 Dover, NJ 07801
1	US Army Laboratory Command ATTN: J. Wells SLCMT-MCZ Materials Technology Laboratory Watertown, MA 02172-0001	1	Commandant US Army Engineer School ATZA-CDD Fort Belvoir, VA 22060
1	Commander US Army Electronics Research & Development Command ATTN: DELSD-L Fort Monmouth, NJ 07703-5301	1	US Army AMCCOM ATTN: Joseph Menke 1032 N. Thornwood Davenport, IA 52804
1	President US Army Aviation Test Board ATTN: STEBG-PO Fort Rucker, AL 36360	1	Commander Headquarters, 39th Engineer Bn (Cbt) Fort Devens, MA 01433
1	US Army Aviation School Library PO Drawer O Fort Rucker, AL 36360	1	President US Army Airborne, Communications & Electronics ATTN: STEBF-ABTD Fort Bragg, NC 28307
1	HQ 193D Infantry Brigade (Panama) ATTN: AFZU-FE APO Miami 34004	1	President US Army Armor and Engineer Board ATTN: ATZK-AE-PD-E Fort Knox, KY 40121-5470
2	Special Forces Detachment, Europe ATTN: PBO APO New York 09050	1	Director ATTN: STSTO-TPP Tobyhanna Army Depot Tobyhanna, PA 18466-5097
2	Engineer Representative USA Research & Standardization Group (Europe) Box 65 FPO 09510	1	Commander and Director USA FESA ATTN: FESA-TS Fort Belvoir, VA 22060
1	Commander Rock Island Arsenal ATTN: SARRI-LPL Rock Island, IL 61299-7300		

1	HQ, USAEUR & Seventh Army Deputy Chief of Staff, Engineer ATTN: AEAEN-MT-P APO New York 09403
1	Director US Army TRADOC Systems Analysis Activity ATTN: ATAA-SL (Tech Library) White Sands Missile Range, NM 88002

BELVOIR RD&E CENTER

Circulate
1	Commander STRBE-Z Deputy Commander STRBE-ZD Technical Director STRBE-ZT Assoc Tech Dir (E&A) STRBE-ZTE Assoc Tech Dir (R&D) STRBE-ZTR Executive Officer STRBE-ZX Sergeant Major STRBE-ZM Advanced Systems Concept Dir STRBE-H Program Planning Div STRBE-HP Foreign Intelligence Div STRBE-HF Systems and Concepts Div STRBE-HC
10	STRBE-V
20	STRBE-VF
3	ANQSK-BPG-G
3	Security Ofc (for liaison officers) STRBE-S
2	Tech Library STRBE-BT
1	Public Affairs Ofc STRBE-I
1	Ofc of Chief Counsel STRBE-L

DEPARTMENT OF THE NAVY

1	Director Physics Program (421) Office of Naval Research Arlington, VA 22217
2	Commander Naval Facilities Engineering Command Department of the Navy ATTN: Code 032-B 062 200 Stovall Street Alexandria, VA 22332

1	US Naval Oceanographic Office Navy Library/NSTL Station Bay St. Louis, MO 39522
1	Library (Code L08A) Civil Engineering Laboratory Naval Construction Battalion Center Port Hueneme, CA 93043
1	Director Earth Physics Program Code 464 Office of Naval Research Arlington, VA 22217
1	Naval Training Equipment Center ATTN: Technical Library Orlando, FL 32813
3	Naval Sea Systems Command ATTN: P. Schneider PMS377J1 Wasington, DC 20362-5101
1	Naval Air Development Center ATTN: V. S. Agarwala, Code 6062 Warminster, PA 18974
3	David W. Taylor Naval Research Center ATTN: A. G. S. Morton Code 2813 Annapolis, MD 21402

DEPARTMENT OF THE AIR FORCE

1	HQ USAF/RDPT ATTN: Commander Washington, DC 20330
1	HQ USAF/PREEU Chief, Utilities Branch Washington, DC 20330
1	HQ Air Force Engineering & Services Ctr Technical Library FL7050 Tyndall AFB, FL 32403

1   US Air Force
     Warner Robins Air Logistics Center
     WR-ALC/MMEM
     Warner-Robins AFB, GA 31098

1   Chief, Lubrications Branch
     Fuels & Lubrications Div
     ATTN: AFWAL/POSL
     Wright-Patterson AFB, OH 45433